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AFATL-TR-76-67

A STUDY OF STYRENE-BUTADIENE RUBBER BLENDS AS IMPROVED FLAME AGENTS

EXPLOSIVES/PROPELLANTS BRANCH
GUNS, ROCKETS AND EXPLOSIVES DIVISION

JUNE 1976

FINAL REPORT: JULY 1973 TO MAY 1974

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Styrene-Butadiene Rubber Blends
Improved Flame Agents

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes a research effort to develop improved flame agents for high velocity over a wide temperature range. The approach taken was to replace the polystyrene in the present Napalm B with another polymer or blend of polymers in order to improve the aerodynamic behavior. This involved a study of the flow behavior of polymer solutions (viscosity and elasticity versus shear rate). The elastic values obtained were correlated with results of air gun tests. Thus, both elasticity and viscosity must be considered when

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evaluating solutions for use as flame agents. The formulations which showed improved flow behavior were various blends and ratios of styrene-butadiene solutions ranging from 27 to 30 percent rubber in gasoline and benzene with the ratio of blending from 1:4 to 4:1 of styrene-butadiene rubber (SBR) 43/40.

PREFACE

This technical report is based on a study conducted during the period from July 1973 to May 1974 at the Air Force Armament Laboratory in support of Project 10820302.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER:

GERALD P. D'ARCY, Colonel, USAF
Chief, Guns, Rockets, & Explosives Division

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SECTION I

INTRODUCTION

The current operational environment for fire bombs requires flame agents that are suitable for use at high delivery speeds and over a wide temperature range. Inadequate performance involves many aspects of the agent's behavior, including poor ignitability and undesirable flow characteristics, particularly at low temperature.

Recent work[1] has shown that materials with comparable shear-dependent flow properties exhibit flow behavior differences in dynamic tests which cannot be accounted for by the observed differences in shear rate degradation.

Gaskins[2] first pointed out the importance of considering both the viscous and elastic behaviors of flame fuels. This work emphasizes the modification of rheological properties of polymer solutions for better survival under high shear stresses and over a wide temperature range.

The blending of various ratios of styrene-butadiene (SBR 43 and SBR 40) resulted in solutions with varying elastic properties as a function of shear rate. These solutions show very little change in viscosity and elastic properties due to temperature differences.

Air gun tests showed varying performances of the various blends which could only be attributed to the elastic property of the polymer solution.

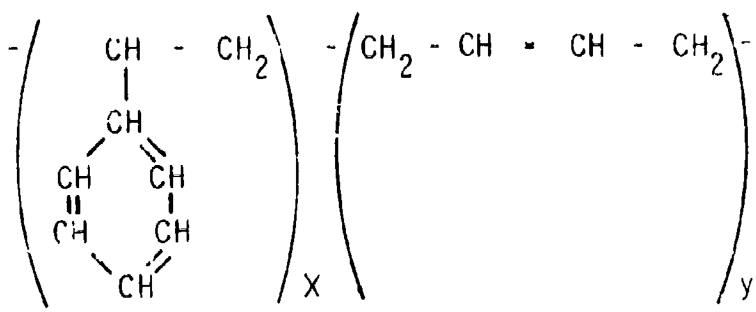
SECTION II

MATERIALS, FORMULATION PREPARATION, AND RHEOLOGICAL CHARACTERIZATION

MATERIALS

The styrene-butadiene rubbers used in this study were supplied by the B.F. Goodrich Chemical Company[a]. The trade name for SBR 40 is Ameripol® 1513 and for SBR 43, Ameripol® 1013. Chemical configuration of styrene-butadiene rubber is given in Figure 1. Solvents used in the formaulations were: benzene, Fisher[a] technical grade; gasoline, government procurement, motor pool grade (Regular) and gasoline simulant (GS), described in AFATL-TR-74-203. GS is formulated from the following Fisher[a] ACS grade chemicals: n-pentane, 40 percent; hexanes 20 percent; isooctane, 5 percent; toluene, 10 percent; xylene, 20 percent; and parafin oil, 5 percent.

I CHEMICAL FORMULA



	STYRENE	BUTADIENE
SBR 40	40%	60%
SBR 43	43%	57%

II FLAME FUEL FORMULATION

30% SBR BLEND OF 20% SBR 43, 10% SBR 40

42.5% GASOLINE (MOTOR POOL GRADE)

27.5% BENZENE (TECHNICAL GRADE)

Figure 1. Styrene-Butadiene Rubber (SBR) Formulation

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[a] Use of these commercial products in carrying out the experiments required by this study does not constitute or imply an indorsement of the products by the US Government.

FORMULATION PREPARATION

The polymer solutions were formulated by adding the appropriate chemicals into glass jars, sealing, and then placing the jars on a slowly rotating wheel. The solution concentrations ranged from 25 to 30 percent, with varying ratios of SBR 40 and SBR 43 (Table 1). In all solutions, the solvents were gasoline and benzene or gasoline simulant (GS) and benzene in the ratio of 1.6 to 1.

All formulations were weighed at the time of preparation and reweighed before rheological testing to assure no loss of volatile solvents

TABLE 1. RHEOLOGICAL STUDY OF SBR BLENDS

Ratio and Percentage Studied at 32^{o} F and 75^{o} F	
Polymer Percent	Ratio Blend of SBR 43/40
25	1:1, 1:2, 2:1, 1:4, 4:1
27	1:1, 1:2, 2:1, 1:4, 4:1
29	1:1, 1:2, 2:1, 1:4, 4:1
30	1:5, 5:1 1:1, 1:2, 2:1, 1:4, 4:1, 3:2

RHEOLOGICAL CHARACTERIZATION

The flow data generated during this study was obtained using a Model 3501 Capillary Extrusion Rheometer, Monsanto Research Corporation, equipped with a refrigerated barrel and set-point controllers to permit measurements at temperatures as low as -4^{o} C (24.8^{o} F). This instrument is capable of measuring shear rates between $10^{1}sec^{-1}$ and $10^{6}sec^{-1}$, depending upon the material being tested.

The data obtained were reduced using a computer program which assumed power law flow and also applied the Rabinowitsch correction for wall effects. The output of this program was shear stress (τ), corrected viscosity (η_{α}), corrected shear rate ($\dot{\gamma}_{\omega}$), and percent memory (elasticity). Memory is directly related to the fundamental term of recoverable shear, i.e., a measure of the elastic behavior of the material.(3)

From these data curves of viscosity (η_{α}) and percent memory versus shear

rate ($\dot{\gamma}_\omega$) were constructed. The viscosity curves were fitted to a least squares analysis for a best straight line. (See Reference 4 for a detailed description of the program and terms above.)

For comparative purposes, the viscosity and memory curves of Napalm B (Air Force standard flame fuel) are included.

SECTION III

RHEOLOGICAL STUDIES OF EXPERIMENTAL BLENDS

SOLUTION RHEOLOGY

The principal objective of the rheology work was to characterize the flow behavior of polymer solutions of varying percentages and blends. This was done by measuring the shear rate dependence of the viscous and elastic characteristics of the solutions.

Previous results indicated that polymer solutions with roughly the same viscosity but different elastic characteristics, exhibited significantly different behavior under aerodynamic stress. Hence, both viscosity and memory behavior for the various concentrations and blends of the SBRs were studied at varying shear rates.

Table 1, represents the various formulation concentrations and blends measured during this study. Data for all these blends did not appear worthy of publication. The average flow data (viscosity versus shear rate) obtained for some of these concentrations are presented in Figures 2 and 3 at 23.8° C (75° F) and 0° C (32° F). The memory versus shear rate ($\dot{\gamma}_\omega$) obtained for these concentrations are presented in Figures 4 through 7 at 23.8° C (75° F).

This data clearly shows that viscosity and memory varies with temperature much more for thermoplastic polymer solutions (Napalm B type) than for rubber-based solutions, such as the SBR's. From earlier tests, indications were that a solution of lower memory than SBR 43 was desirable, so several variations of the blends were investigated in the search for an agent which could provide a degree of flexibility in elastic behavior without appreciably affecting the viscosity.

VISCOSITY

The purpose of the study was to obtain a solution with the best flow properties through blending of the SBR 43 and SBR 40 polymers in varying ratios and/or percentages. The SBR materials were investigated because of their temperature-insensitive characteristic.

Figures 8 and 9 represent the data acquired on formulations of 27 percent to 32 percent SBR 40 and SBR 43 over a temperature range of 0° C (32° F) and 23.9° C (75° F). The change in viscosity for the various SBR concentrations over this temperatu.e range is thus found to be quite small at low shear rates.

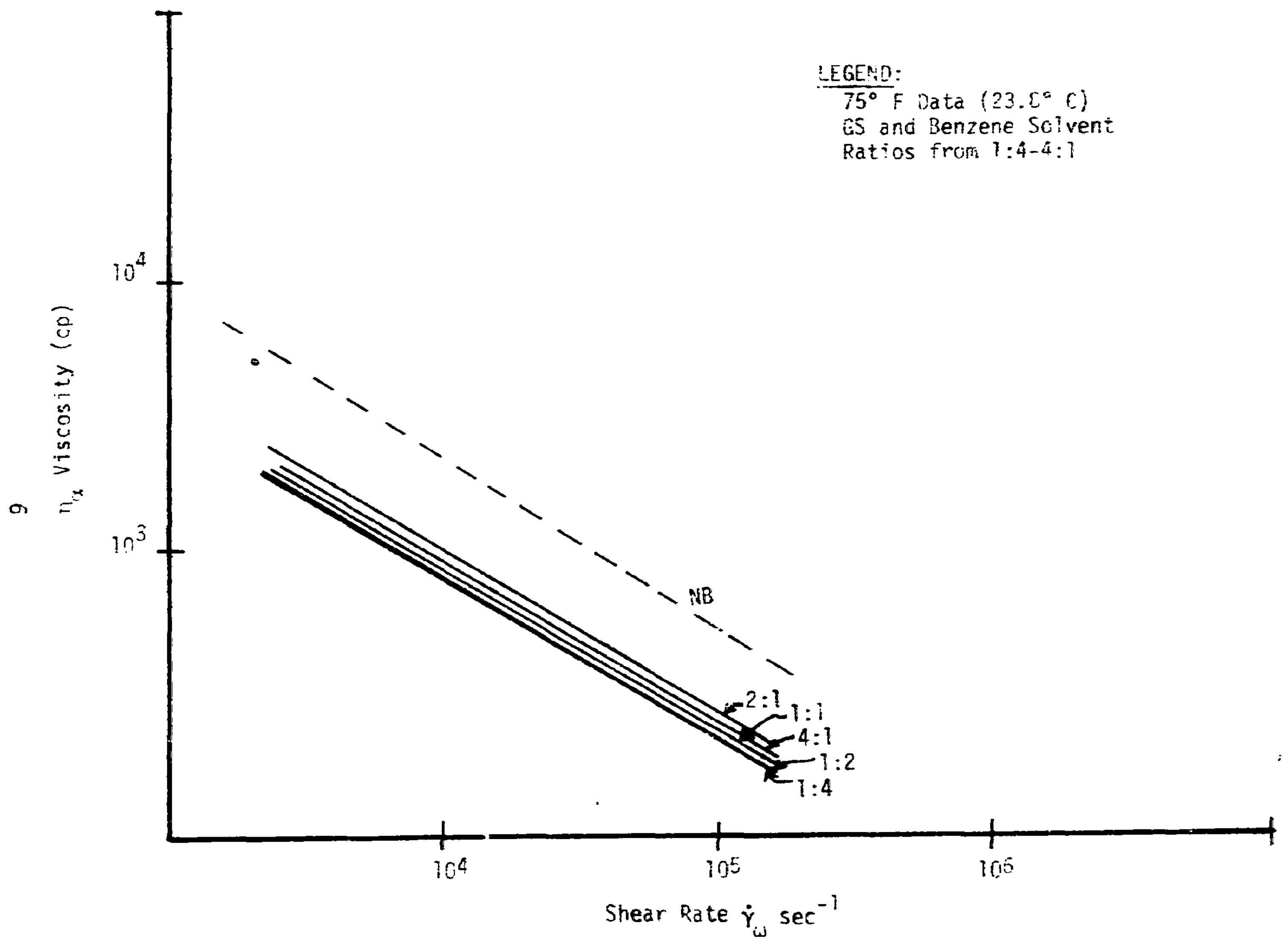

Figure 2. Average Viscosity of SBR Concentrations of 25 to 30 Percent at Various Ratios

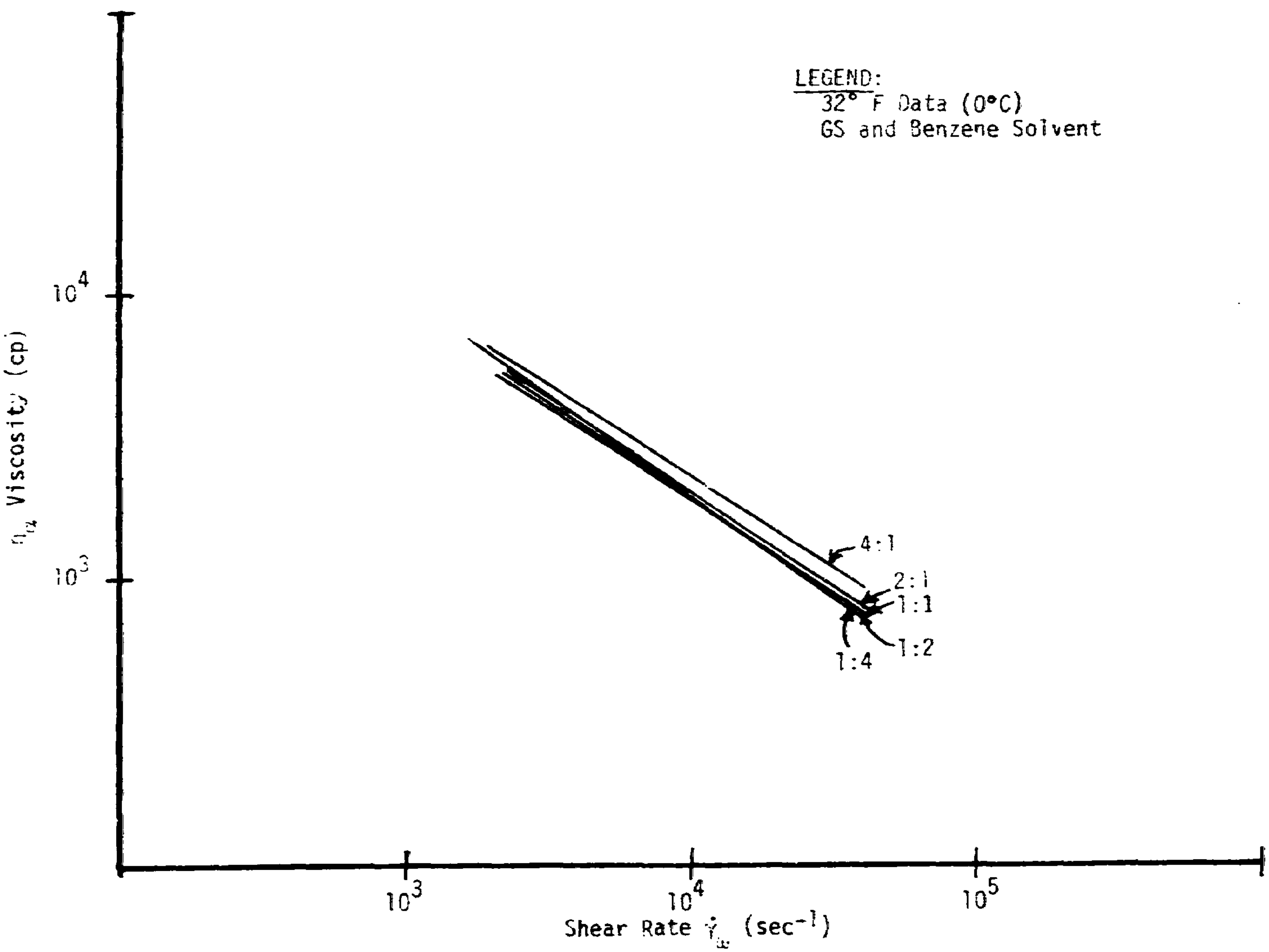

Figure 3. Average Viscosity of SBR 43/40 in Concentrations of 27 to 30 Percent, at 4:1-1:4 Ratios

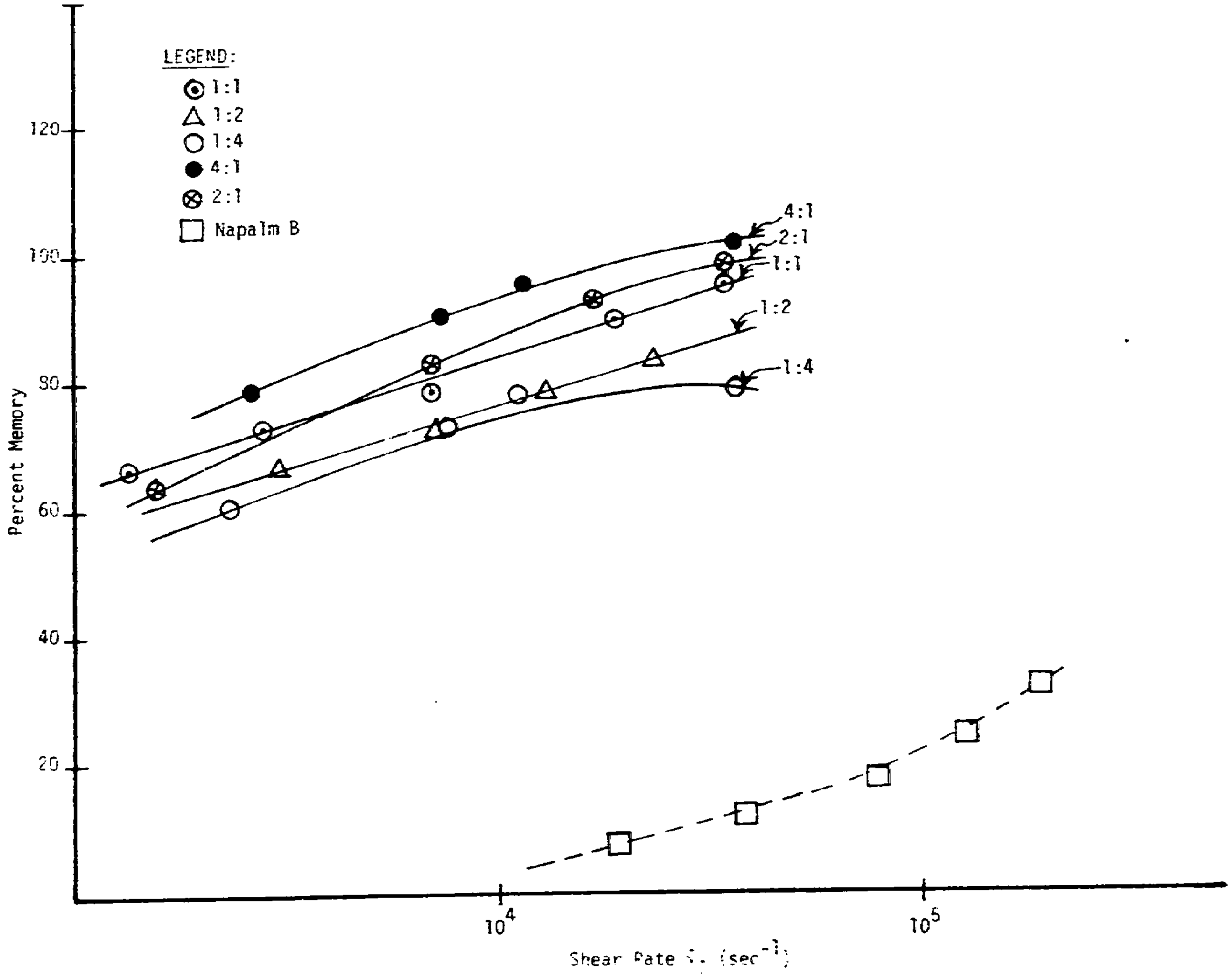

Figure 4. Percent Memory of 30 Percent SBR 43/40 in GS and Benzene at 23.8° C

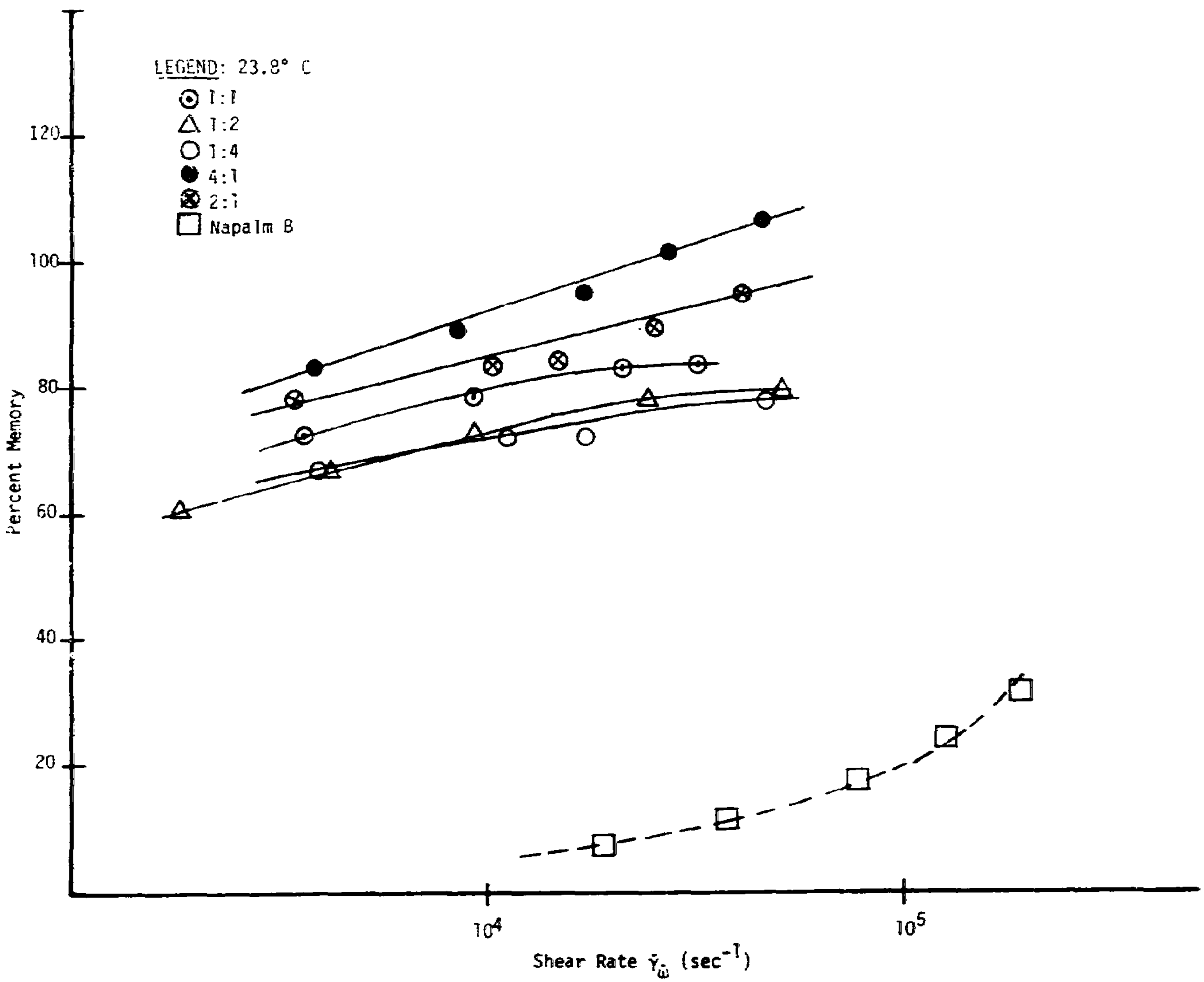

Figure 5. Percent Memory of 29 Percent SBR 43/40 in GS and Benzene at 23.8° C

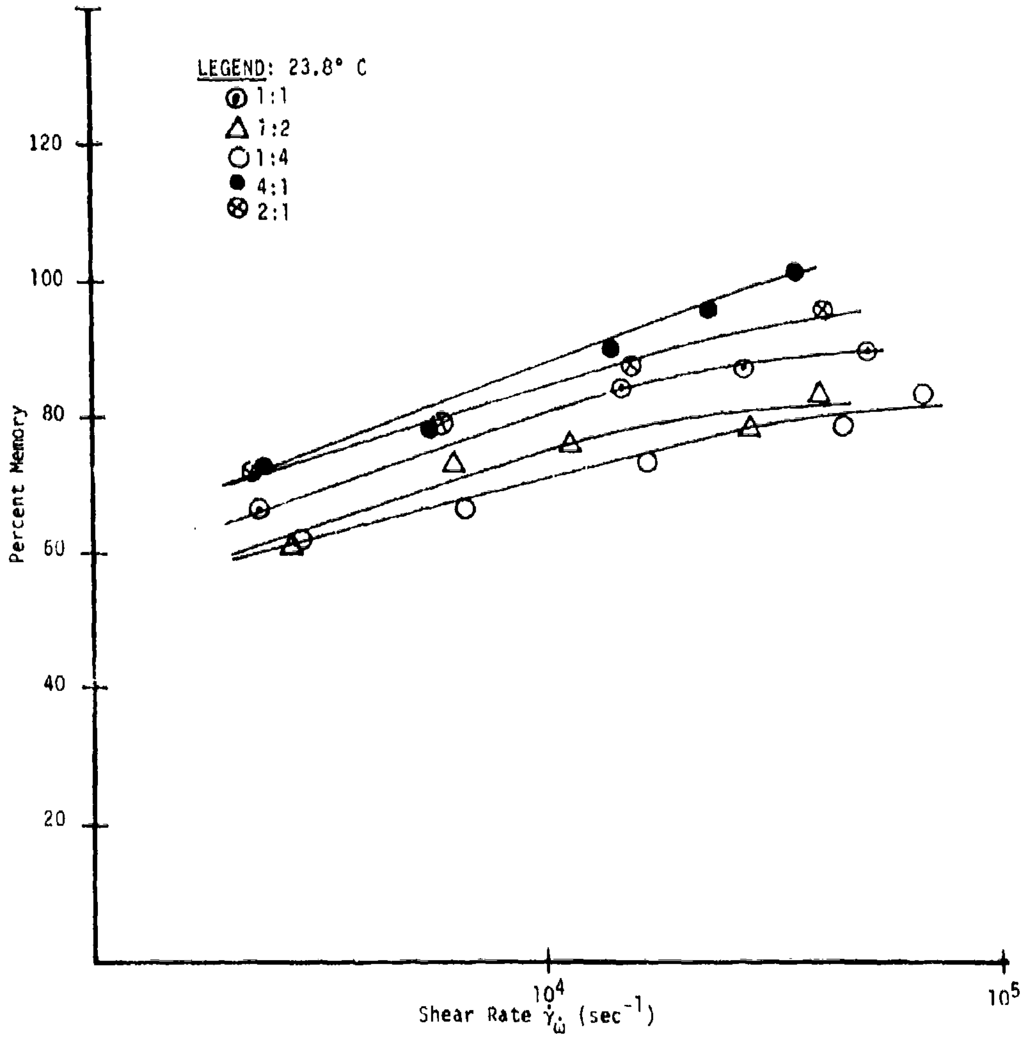

Figure 6. Percent Memory of 27 Percent SBR 43/40 in GS and Benzene at 23.8° C

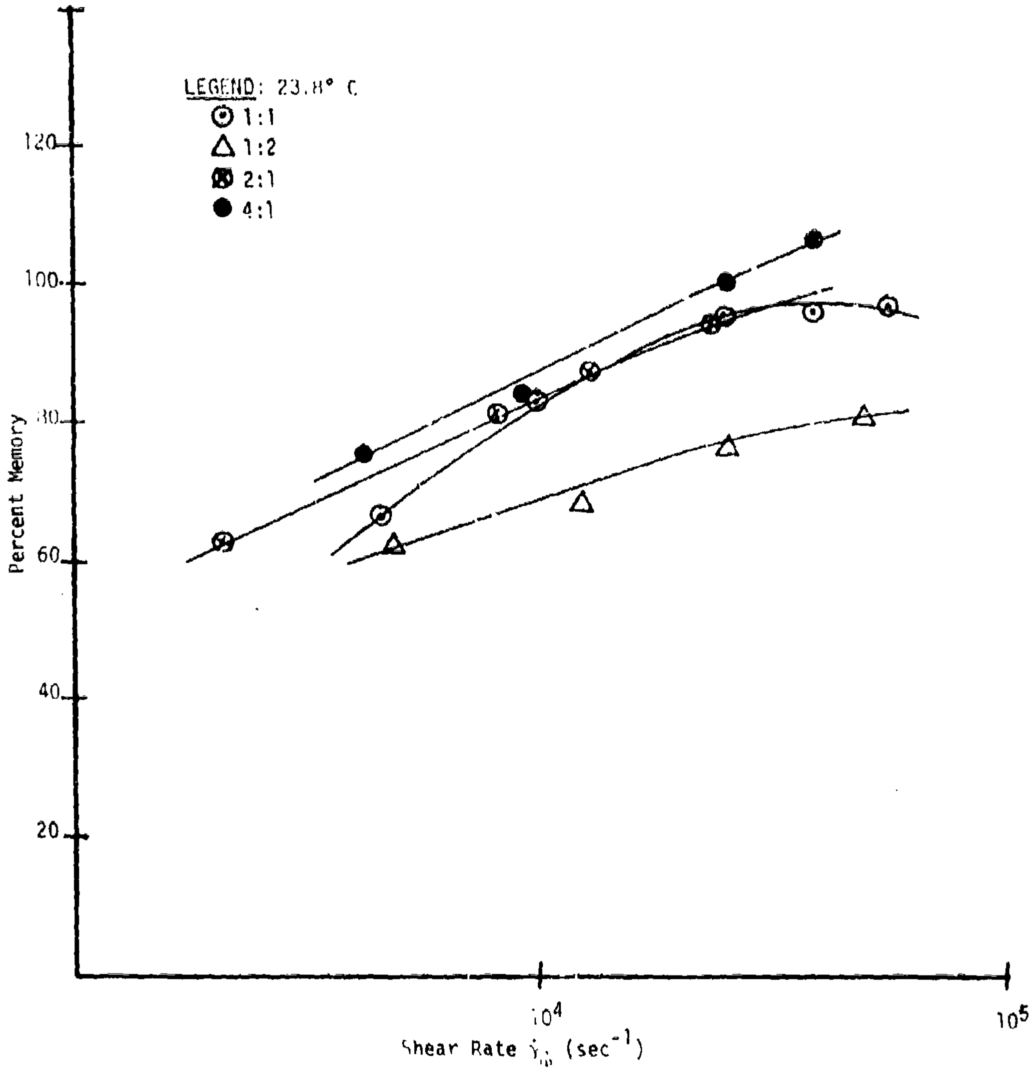

Figure 7. Percent Memory of 25 Percent SBR 43/40 in GS and Benzene at 23.8° C

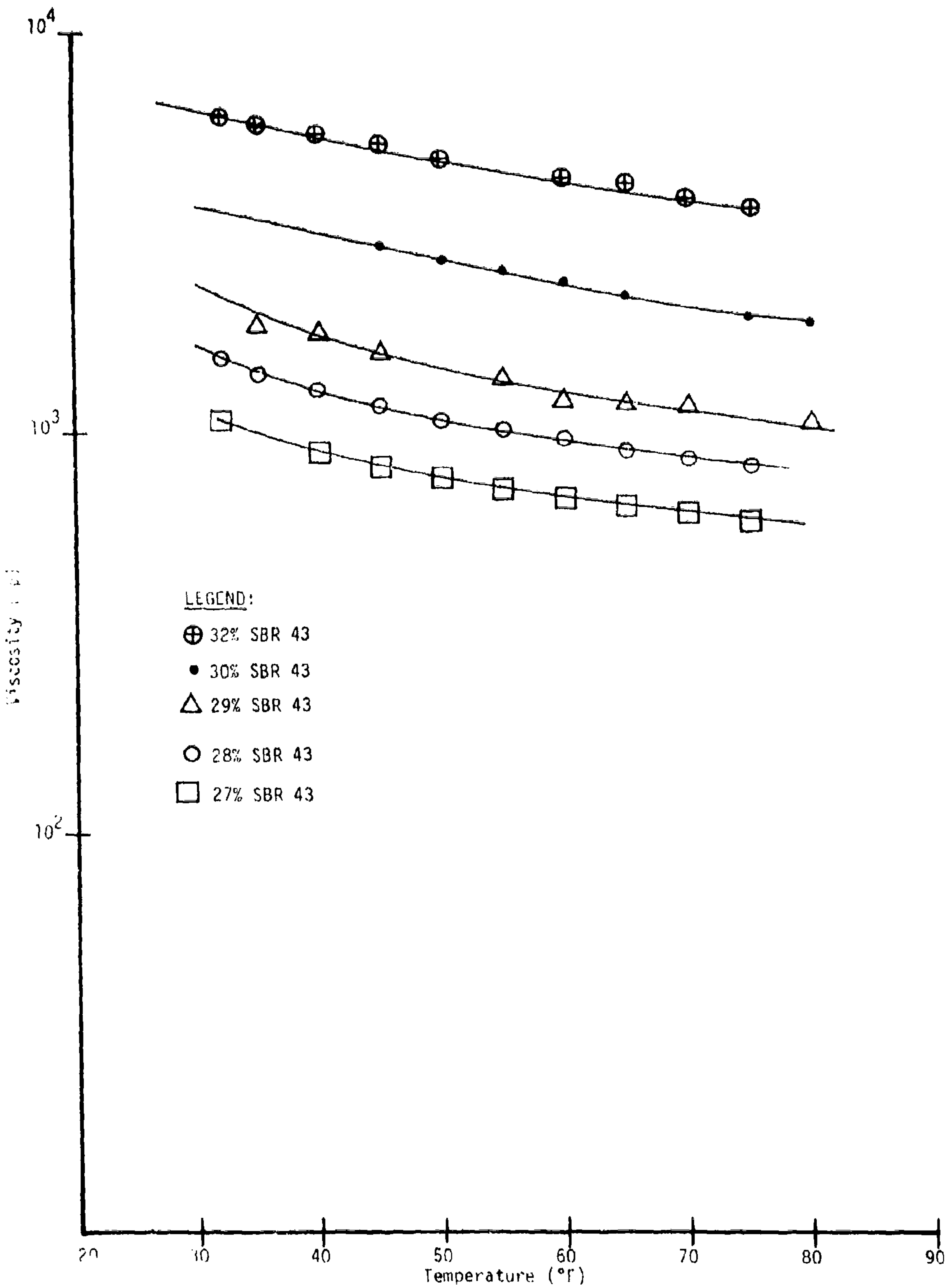

Figure 8. Viscosity of 27-32 Percent SBR 43 Versus Temperature

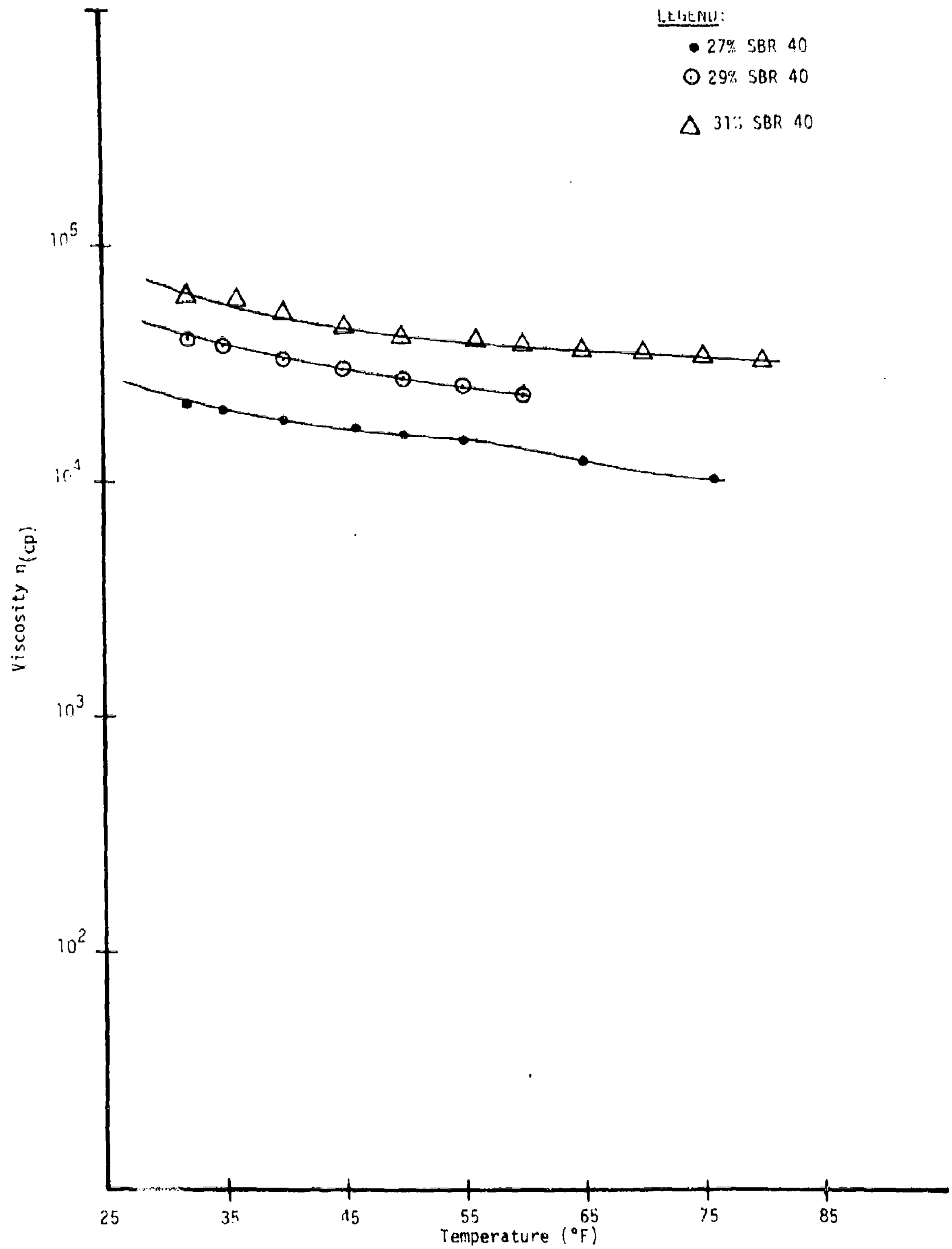

Figure 9. Viscosity of 27, 29, and 31 Percent SBR 40 Versus Temperature

The flow curves of various percentages and blends are presented in Figures 10 through 13; all formulations appear to be comparable in viscosity (η_ω) versus shear rate ($\dot{\gamma}_\omega$) behavior. The greatest variation in viscosity occurs in the 29 to 30 percent concentration with the blend ratio of (1:4) SBR 43/40. The solution showing the greatest shear thinning curve (lowering of viscosity with increased shear rate) was the 29 percent concentration and in the blend ratio of (1:4) SBR 43/40. The highest viscosity was exhibited by the 30 percent concentration and a blend ratio of (5:1) SBR 43/40, which was expected due to the high viscosity of the SBR 43 solution. Very little variation is noted in the flow curves of the 29 percent and 30 percent (2:1) and (1:2) blends; however, when the concentration was reduced to 25 percent polymer, a significant reduction in viscosity was noted in the 1:4 and 1:2 blends, as is shown in Figures 14 and 15.

Comparison of the 0° C (32° F) and 23.8° C (75° F) data (Figures 16 to 19) shows the temperature-insensitive characteristics of the SBR solutions with all percentages exhibiting approximately the same amount of increase in viscosity. The viscosity increase is from 400 centipoise to 800 centipoise over the ranges studied for the 0° C (32° F) data.

PERCENT MEMORY

A previous study[5] has shown the SBR solutions to provide somewhat temperature-insensitive formulations in which memory can be appreciably varied.

Figure 20 presents data for 25 percent SBR 43 at 24° C, 30 percent SBR 43, and 30 percent SBR 40 at -4° C and 24° C. This shows the range of percent memory exhibited by both SBR types.

The foregoing data shows that appreciable differences occur in the elastic behavior of the SBR solutions whose viscous behavior is very similar. Rheological measurements were made on formulations containing SBR 43 and SBR 40. To arrive at an intermediate memory, compositions of ratios varying from 1:5 and 5:1 were formulated and tested.

The rheological studies (flow curves) on formulations incorporating these variations and blends are presented in Figures 21 through 23. The memory data for Napalm B at 23.8° C (75° F) and 0° C (32° F) is also presented in Figure 25 for comparative purposes. It is noted in the Napalm B curves the steep upward slope of the curves with increasing shear rate ($\dot{\gamma}_\omega$). Gaskins[2] proposed that the small elastic characteristic of polystyrene (polymeric constituent of Napalm B) caused it to act as a hard plastic under high shear forces. This leads to the break up into popcorn size particles when Napalm B is disseminated at high aerodynamic speeds.

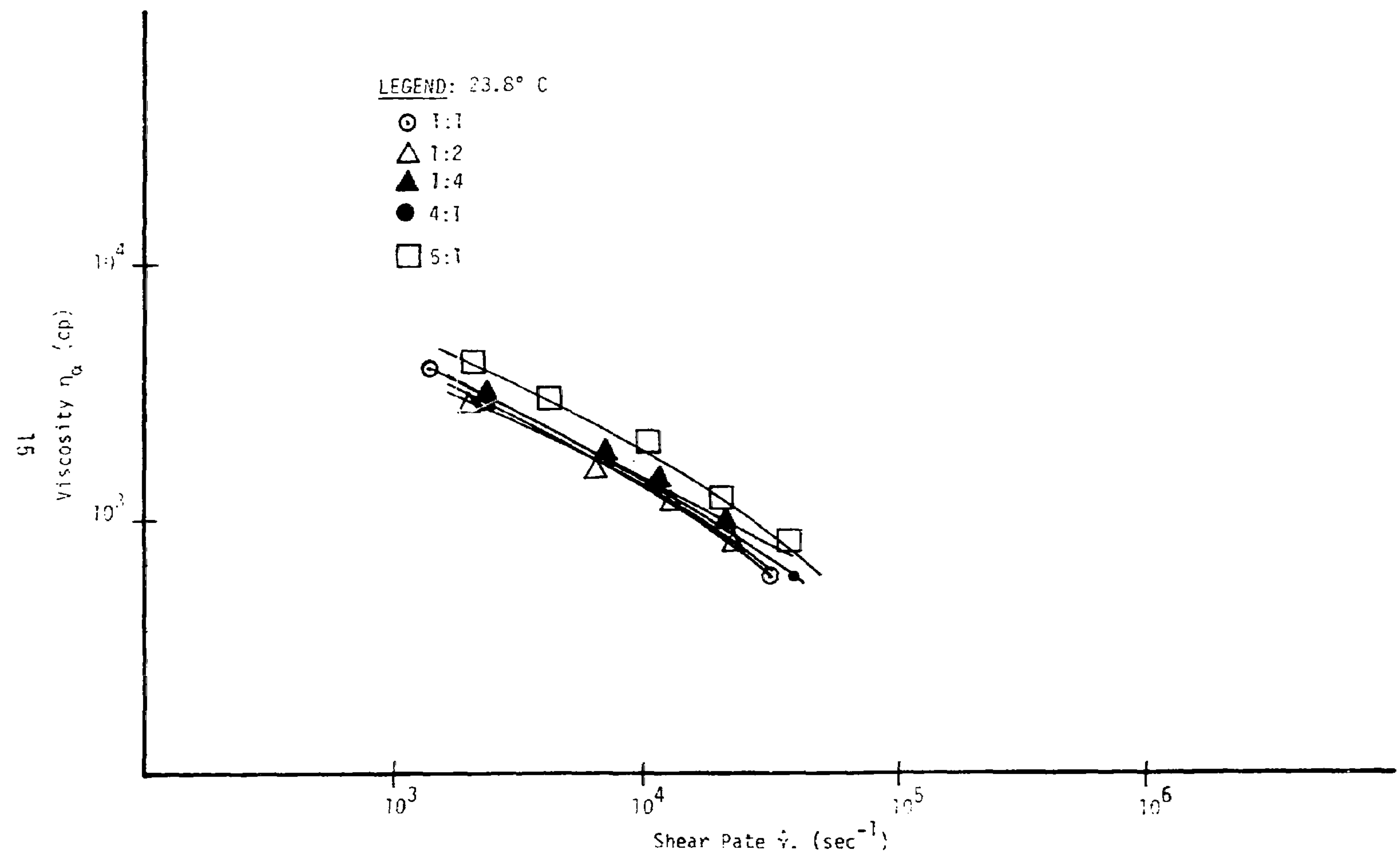

Figure 10. Flow Curve of 30 Percent SBR 43/40 of Various Ratios at 23.8^{o} C

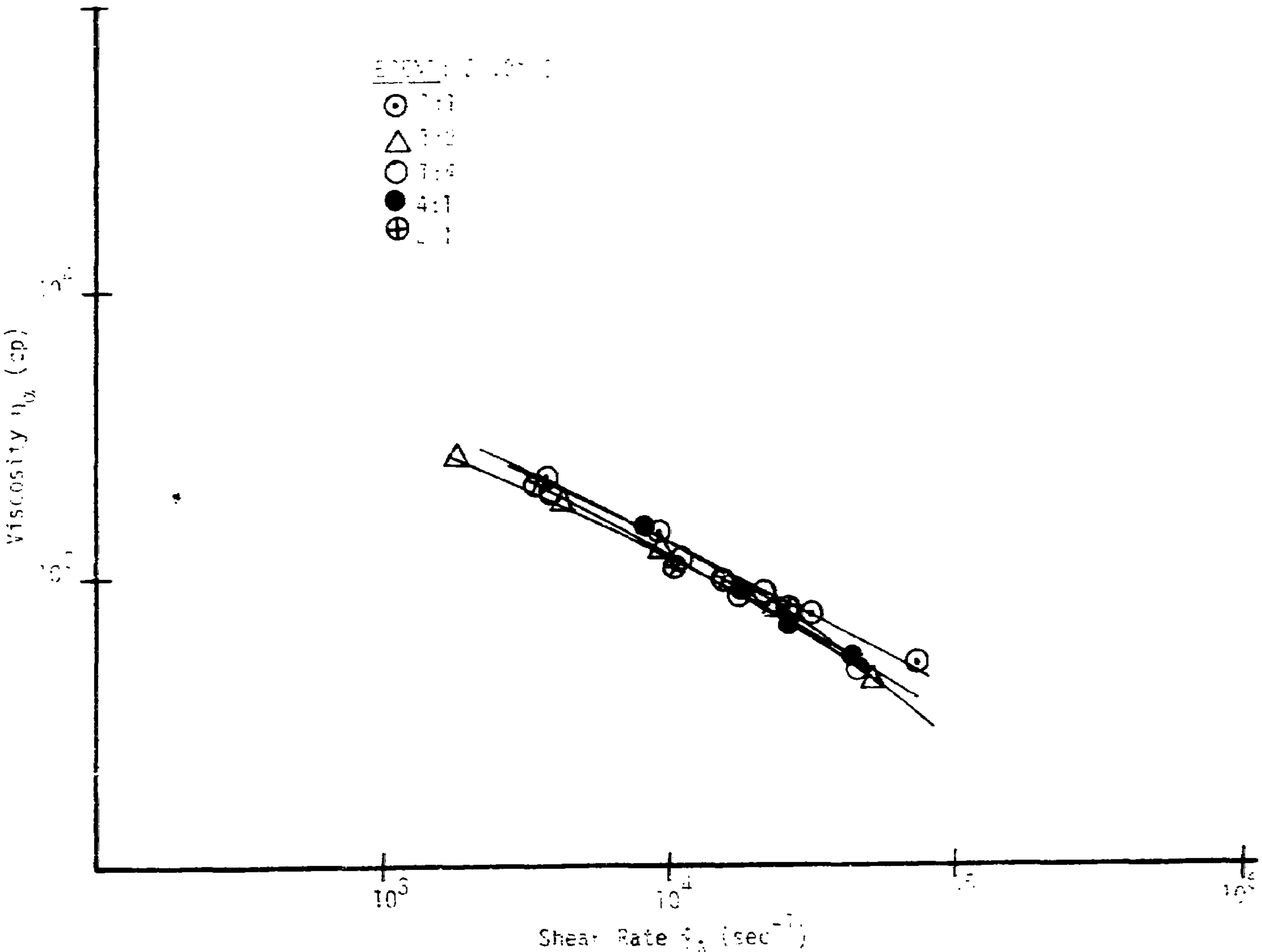

Figure 11. Flow Curve of 29 Percent SBR 43/40 of Various Ratios at 23.9° C

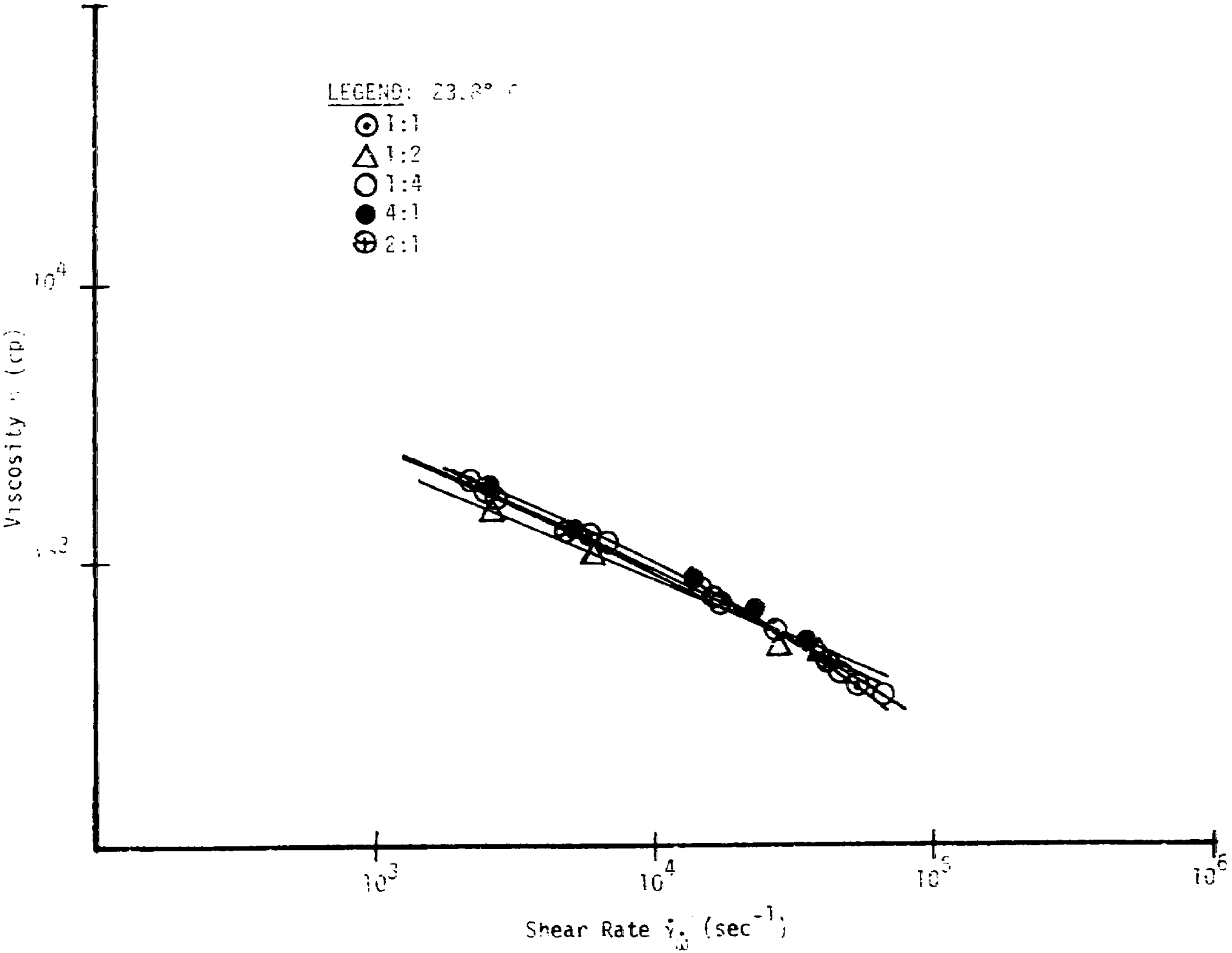

Figure 12. Flow Curve of 27 Percent SBR 43/40 of Various Ratios at 23.8° C

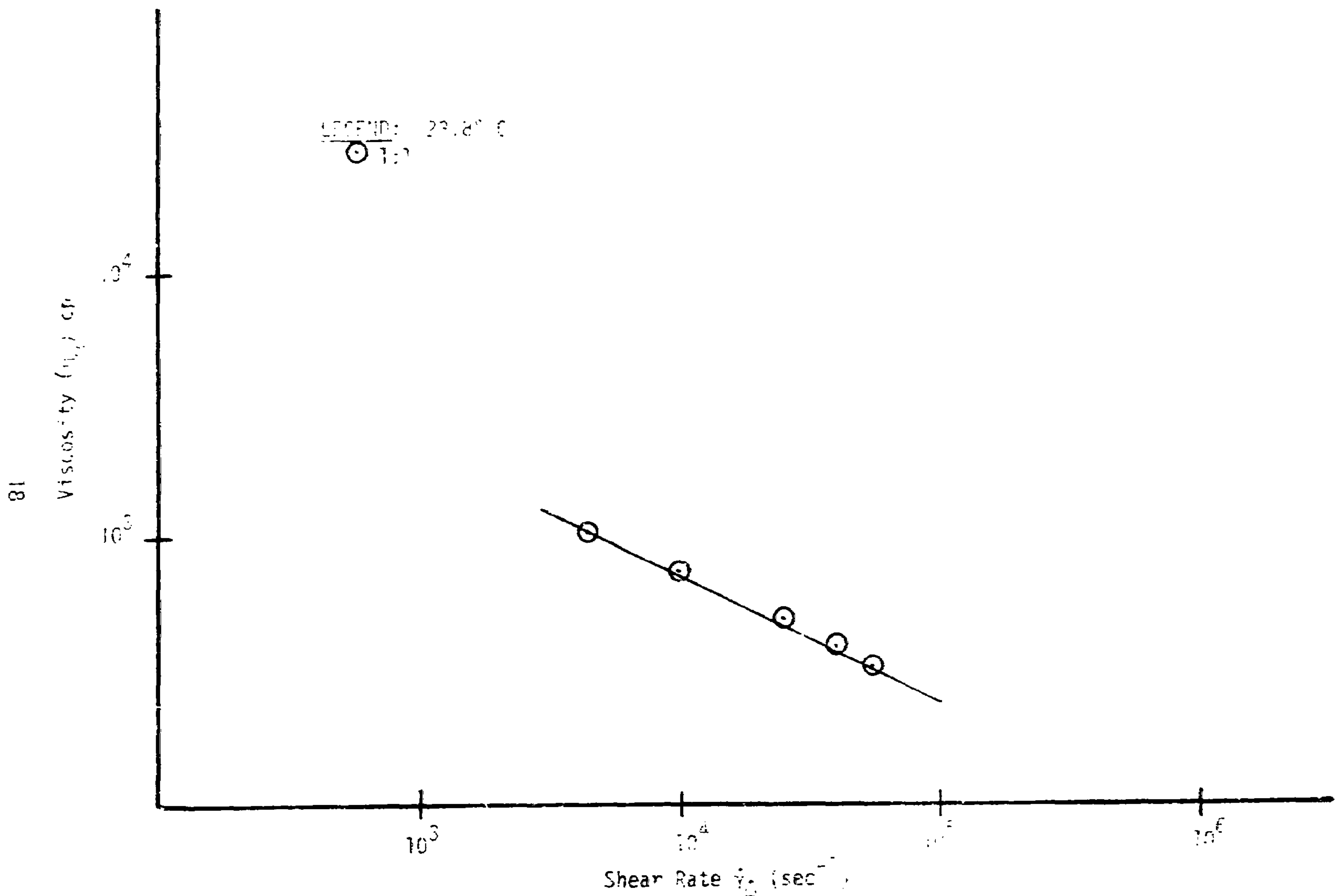

Figure 13. Flow Curve of 25 Percent SBR 43/40 of a 1:1 Ratio at 23.8° C

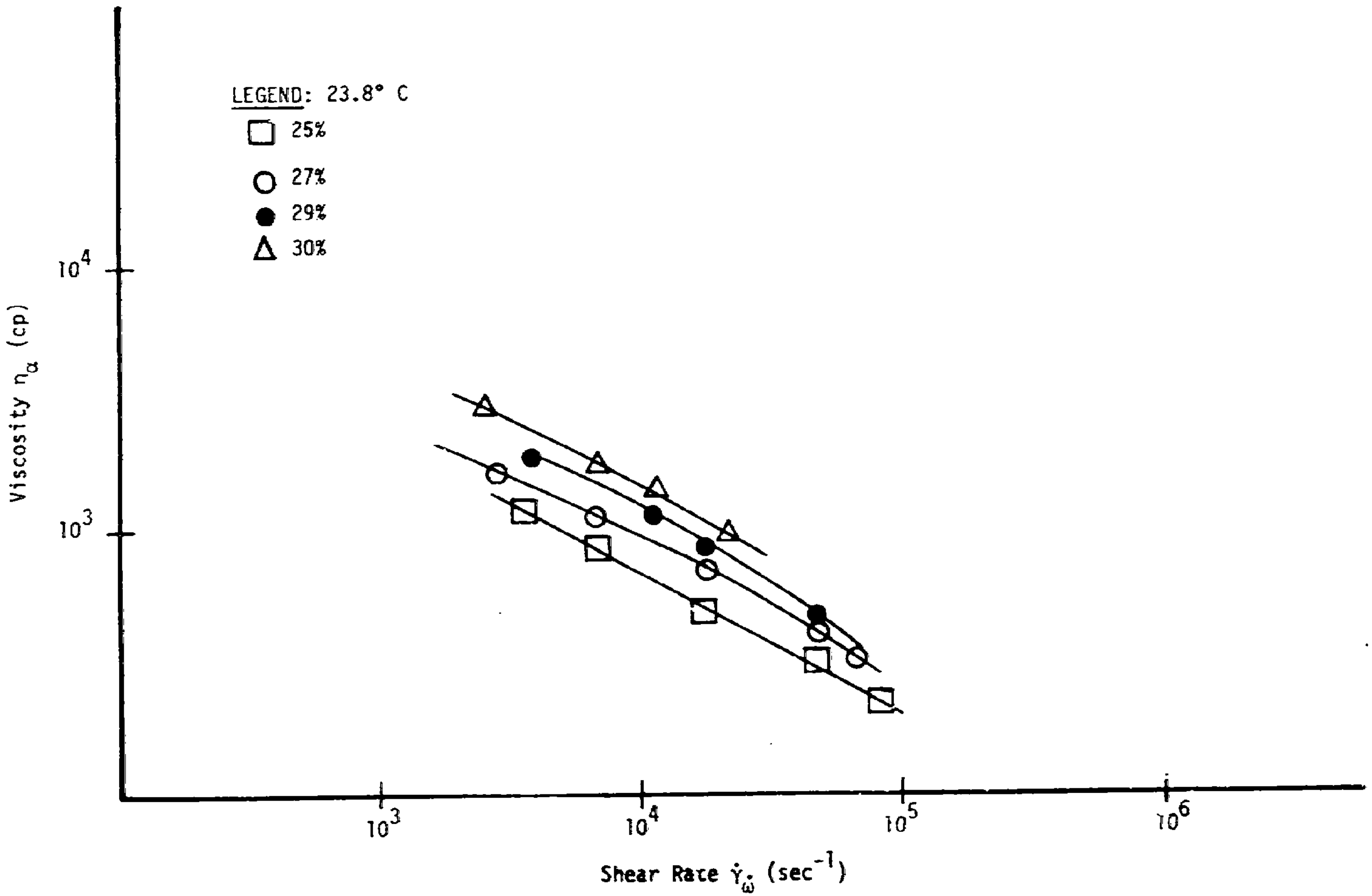

Figure 14. Flow Curves of SBR 43/40, 1:4 Ratios of Various Concentrations

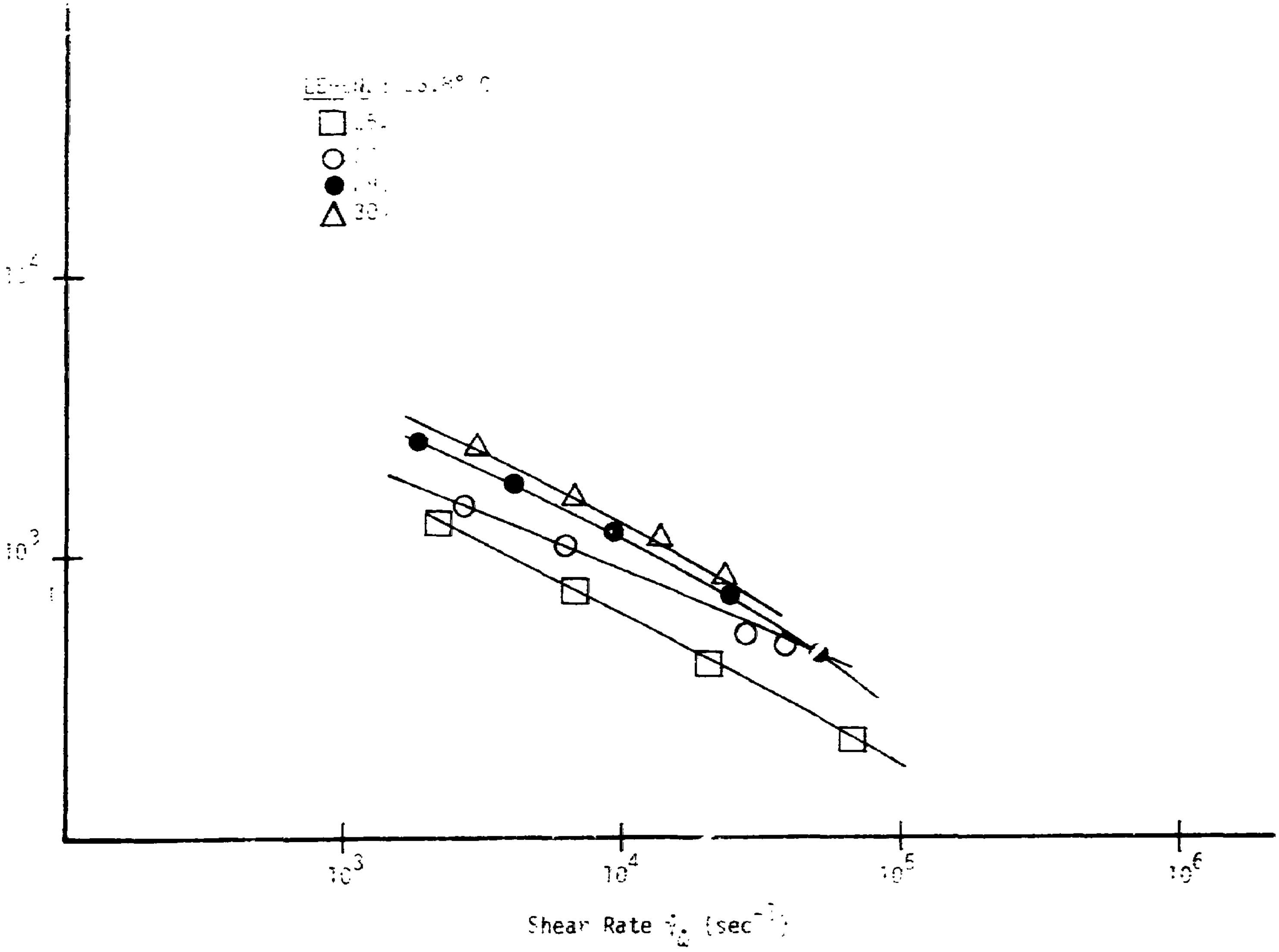

Figure 15. Flow Curves of SBR 43/40, 1:2 Ratio of Various Concentrations

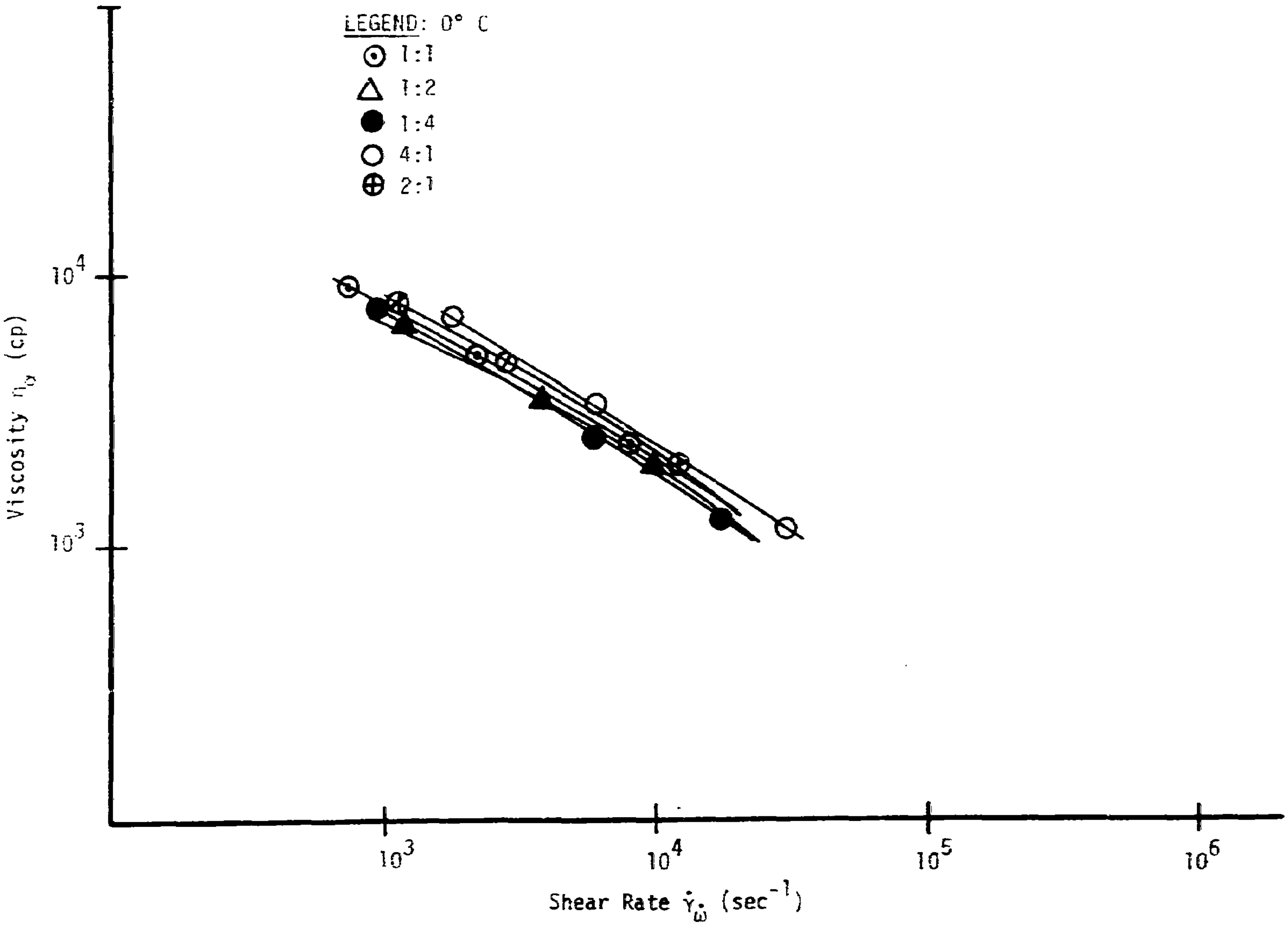

Figure 16. Flow Curves of 30 Percent SBR 43/40 at Various Ratios at 0° C

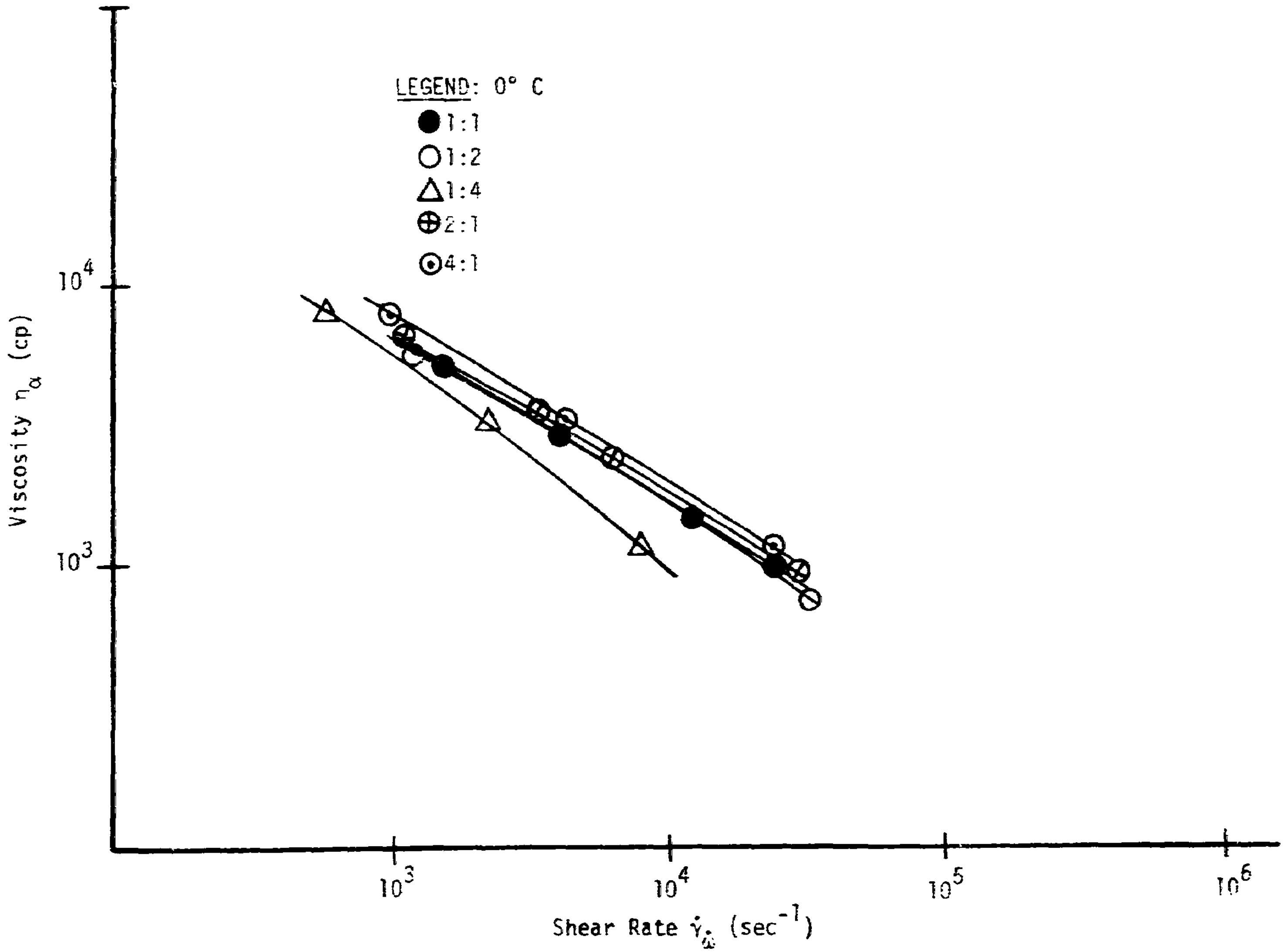

Figure 17. Flow Curves of 29 Percent SBR 43/40 at Various Ratios at 0^0 C

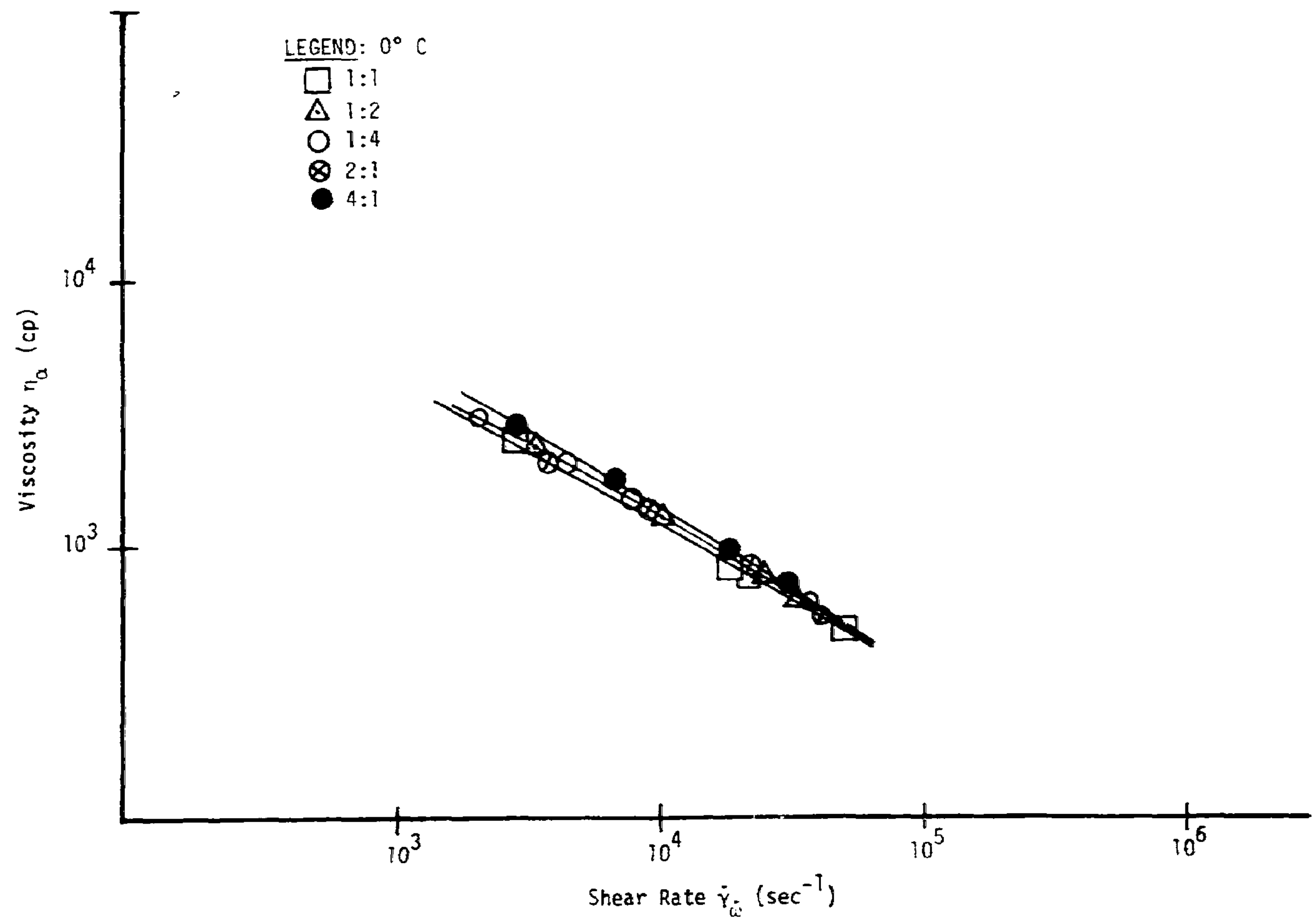

Figure 18. Flow Curves of 27 Percent SBR 43/40 at Various Ratios at 0° C

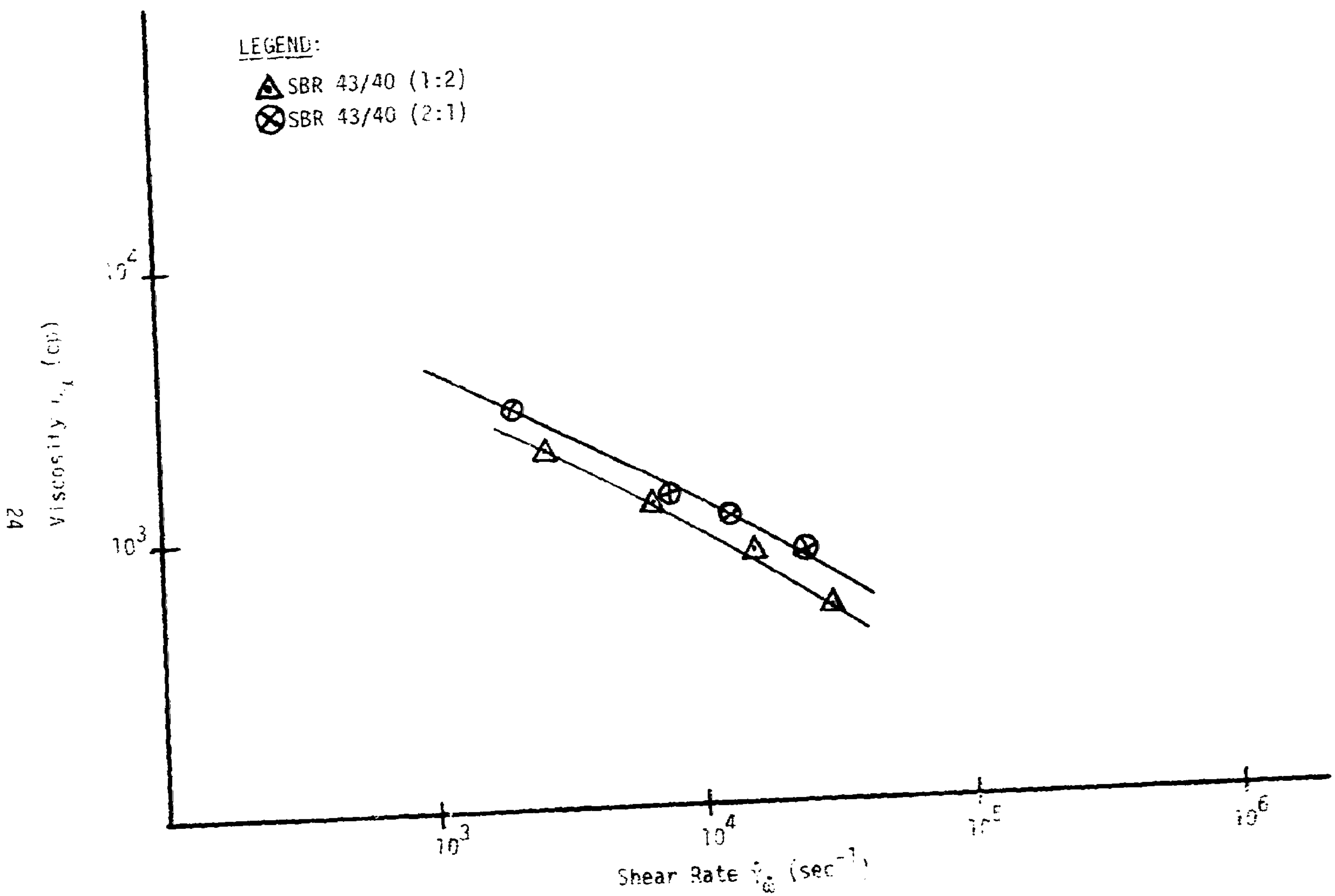

Figure 19. Viscosity of a 25 Percent Concentration of SBR 43/40 at Various Blend Ratios at (320 F) 0° C

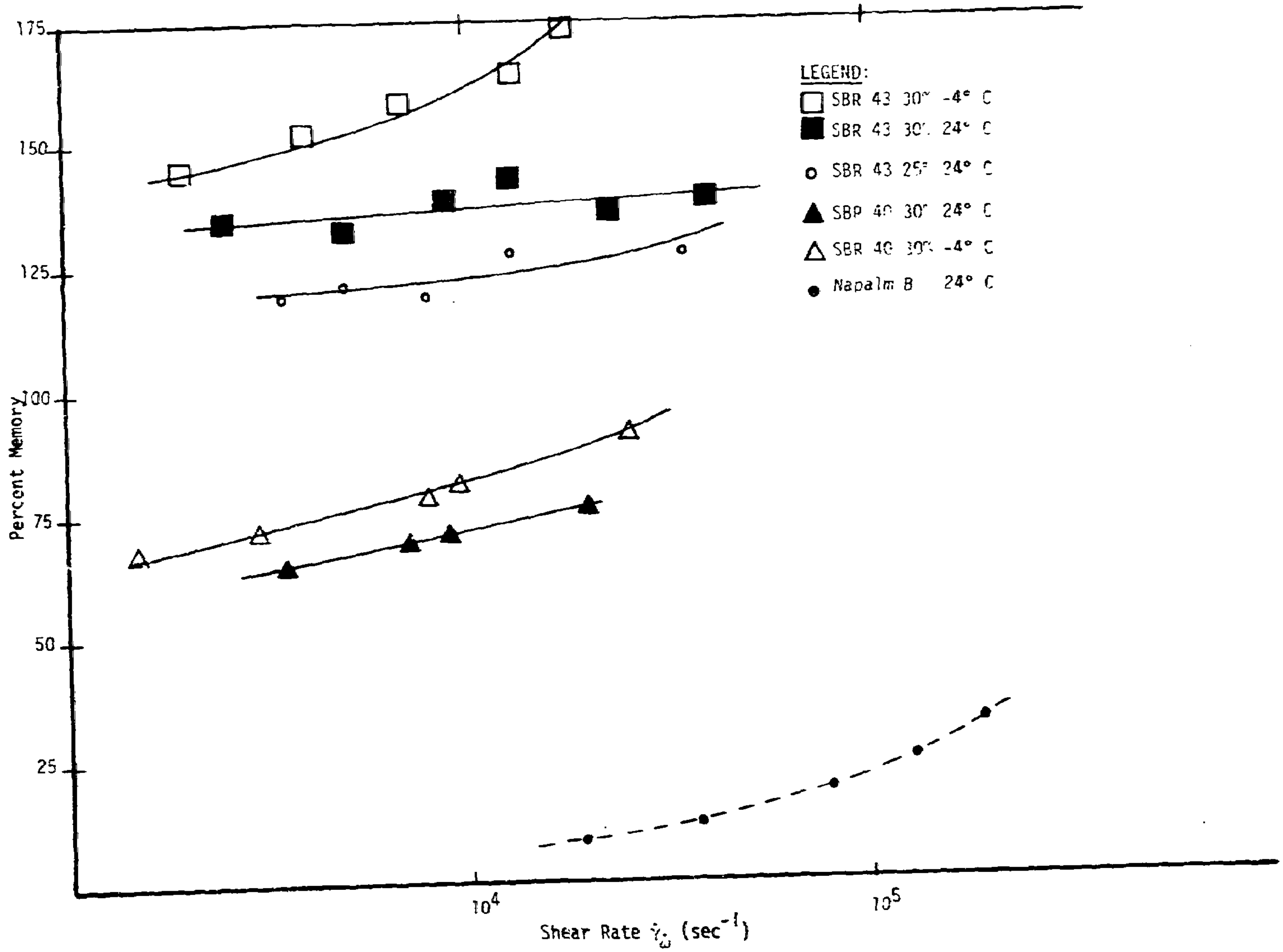

Figure 20. Percent Memory of Various SBR Concentrations at 24^{o} C and -4^{o} C

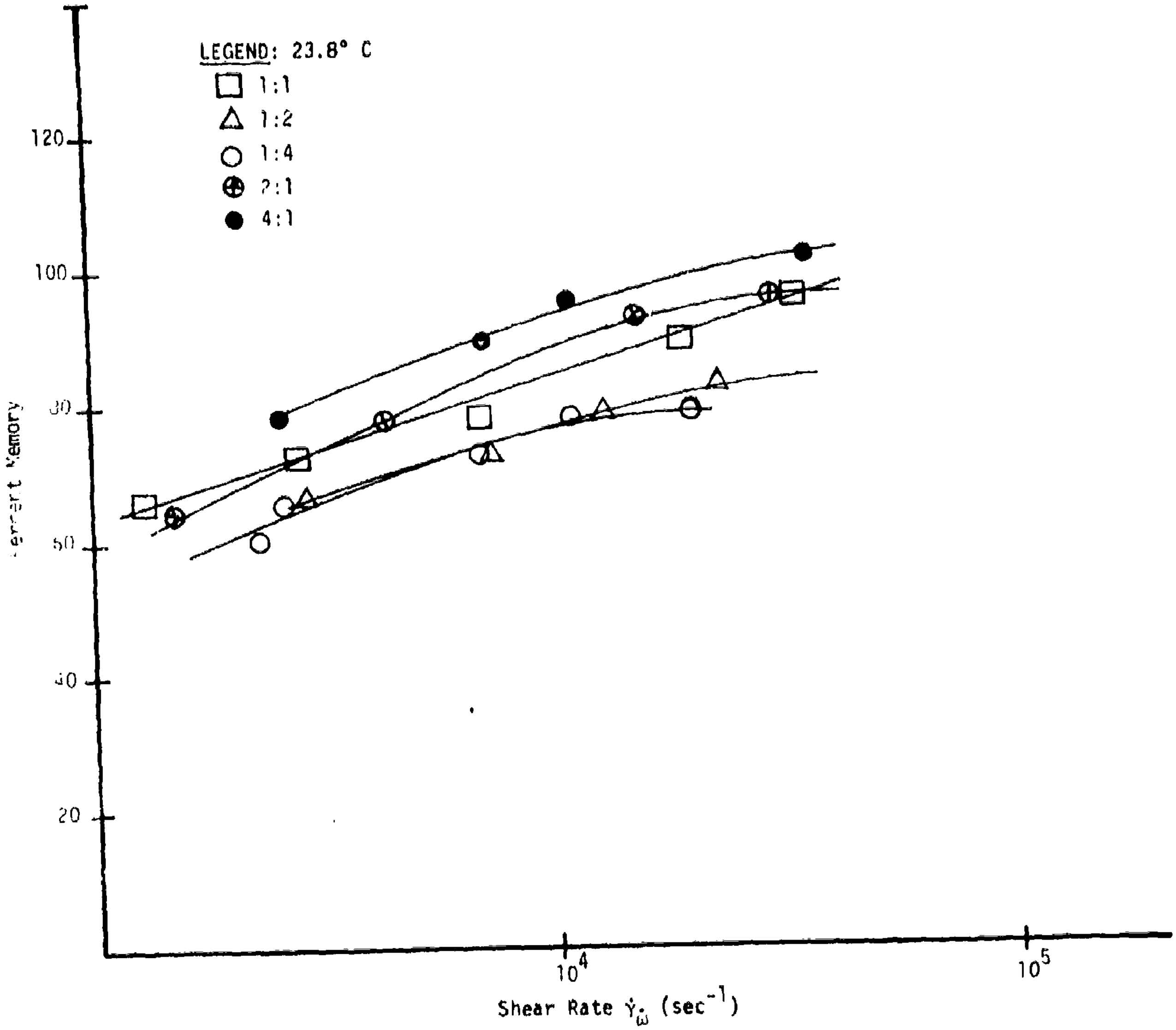

Figure 21. Percent Memory of 30 Percent SBR 43/40 at Various Ratios at 23.8^{0} C

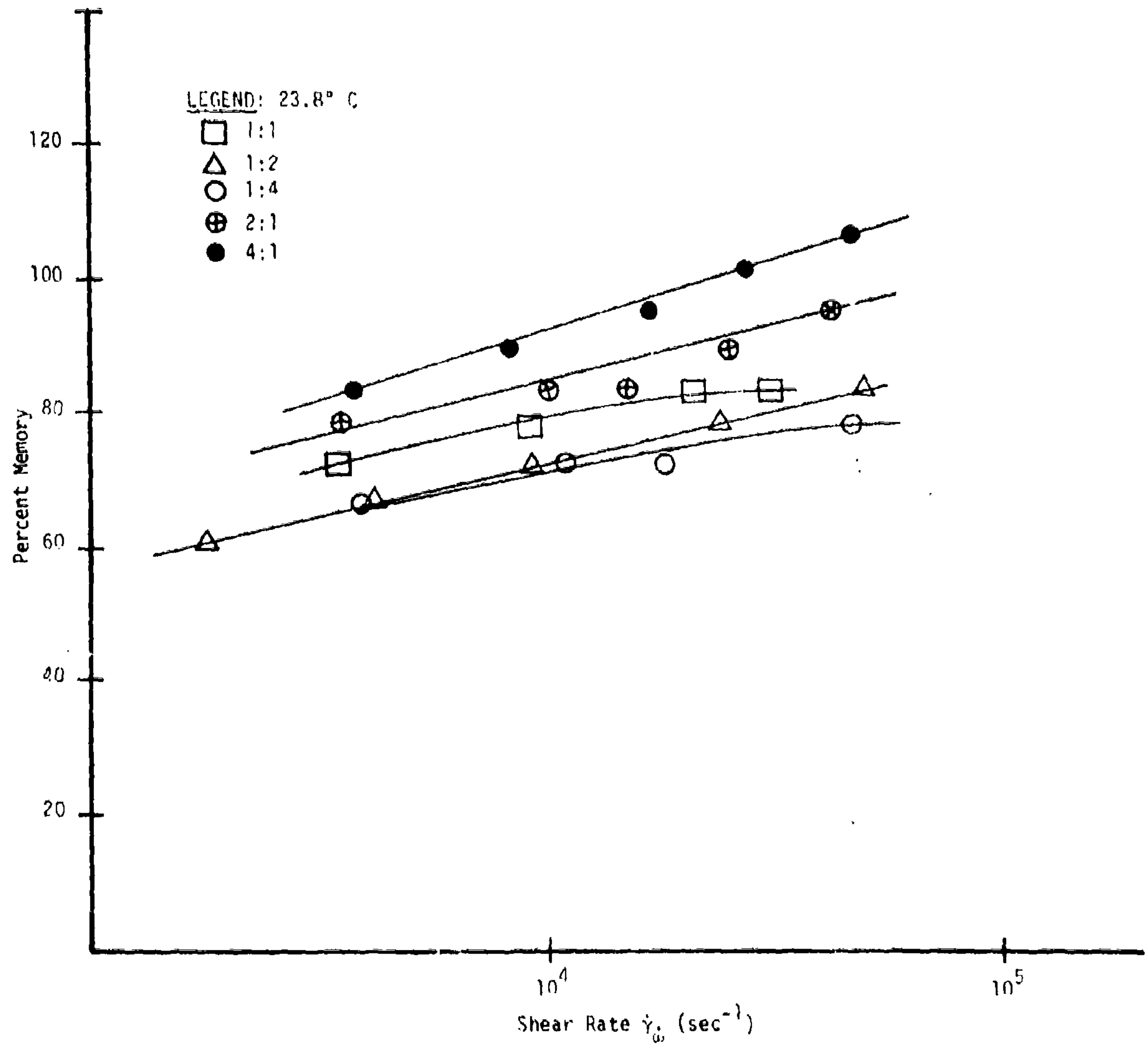

Figure 22. Percent Memory of 29 Percent SBR 43/40 at Various Ratios at 23.8^0 C

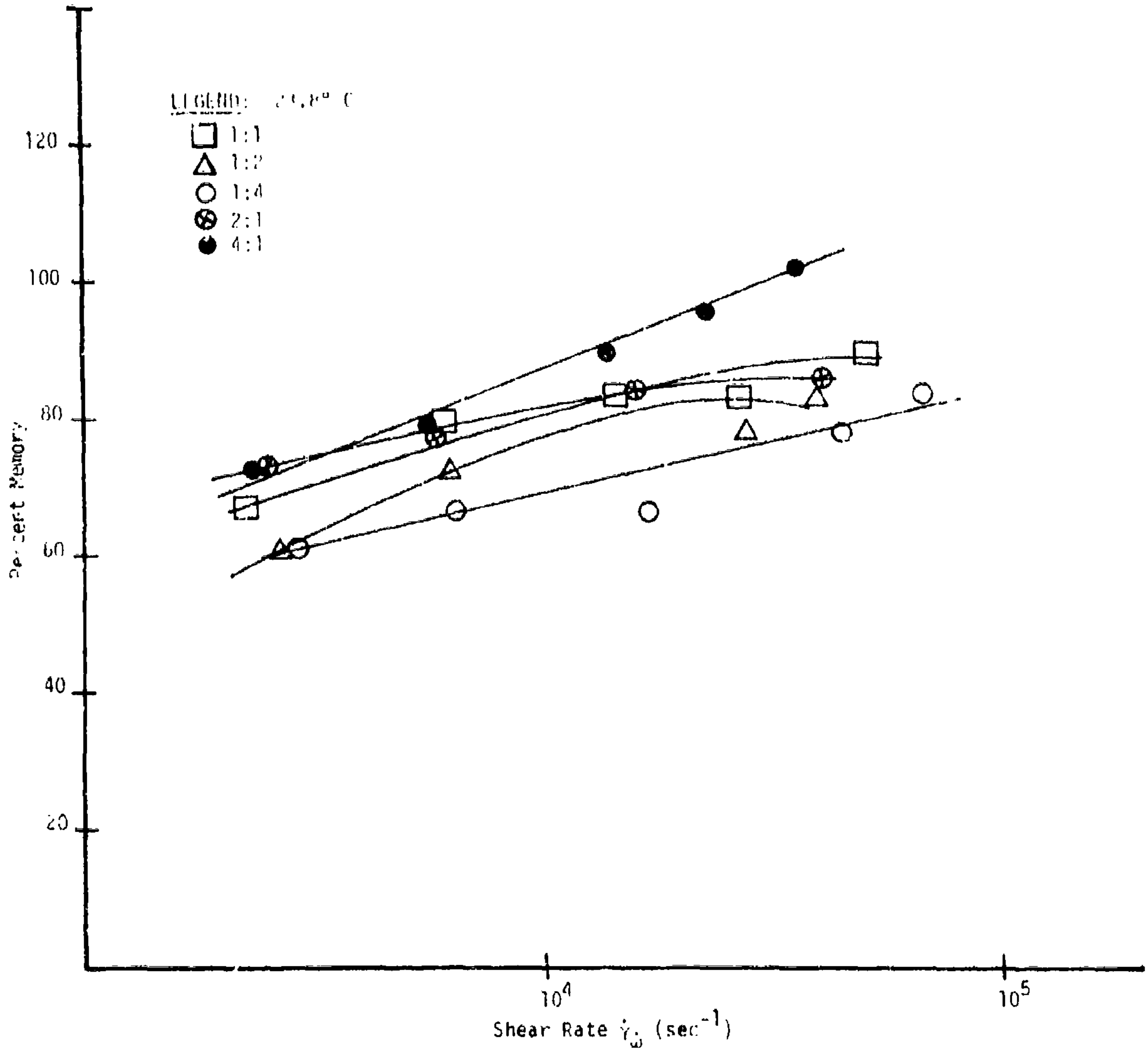

Figure 23. Percent Memory of 27 Percent SBR 43/40 at Various Ratios at 23.8^0 C

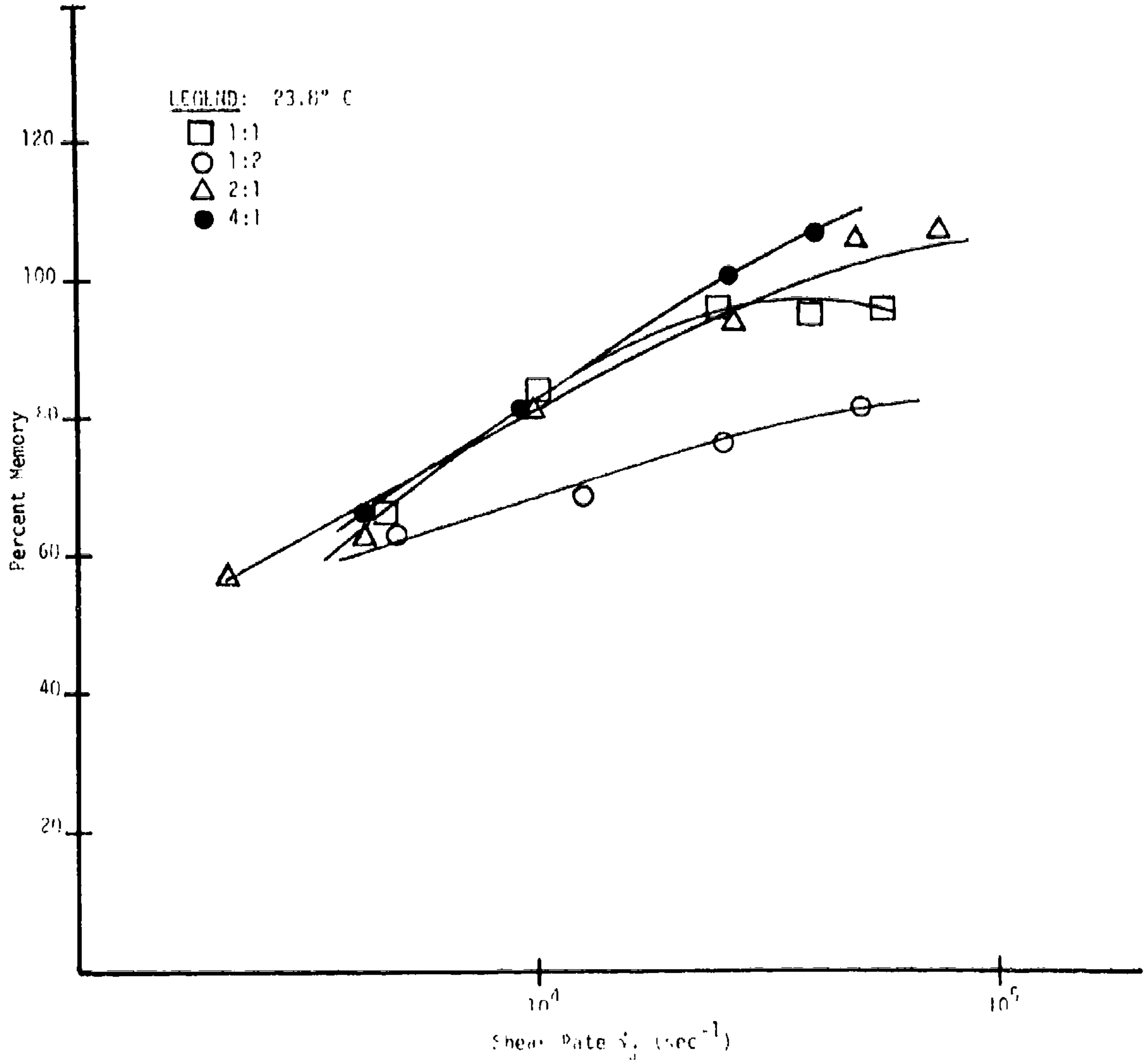

Figure 24. Percent Memory of 25 Percent SBR 43/40 at Various Ratios at 23.8^{0} C

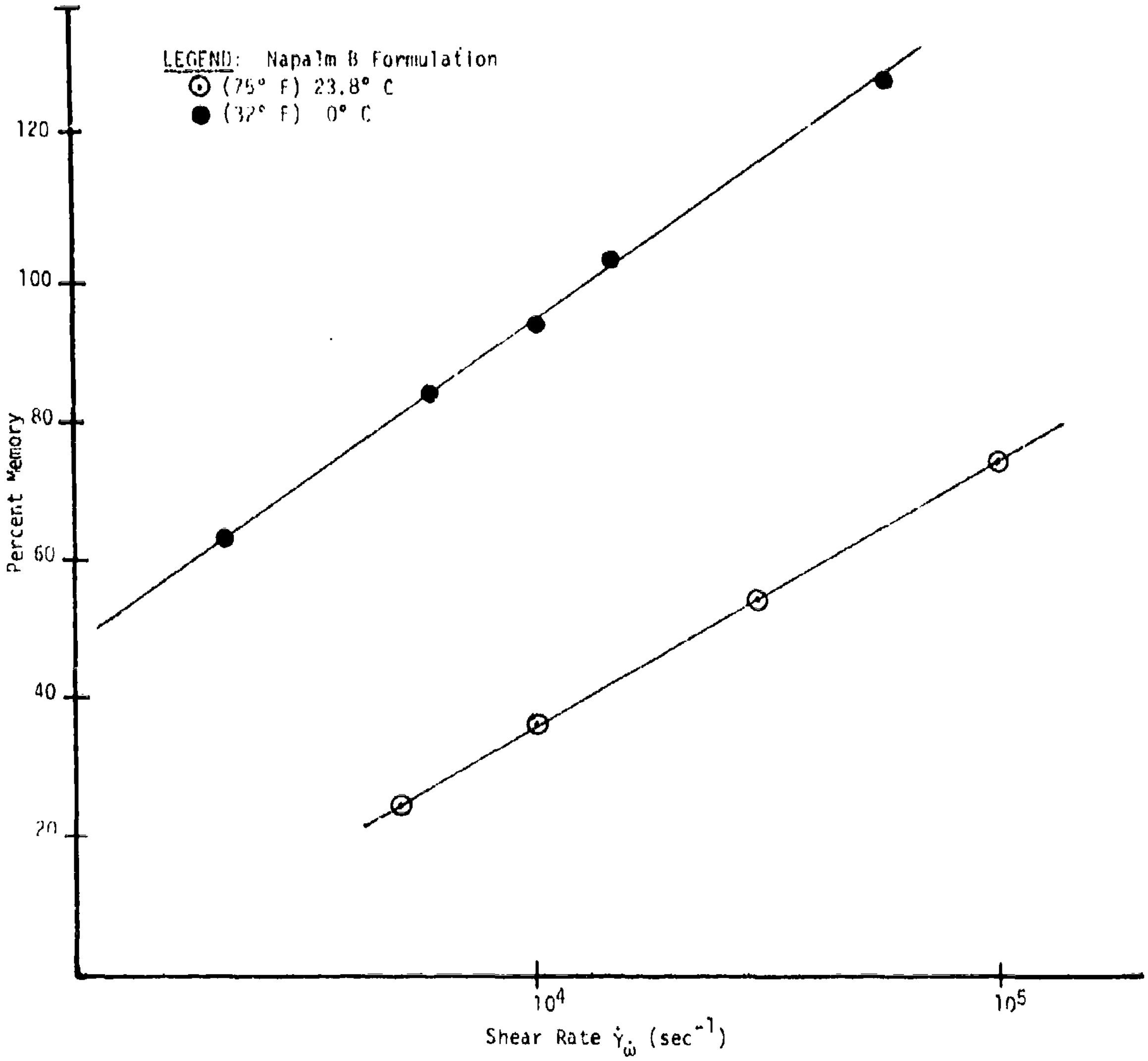

Figure 25. Percent Memory of Napalm B at 23.8° C and 0° C

Figure 24 presents data for the 25 percent SBR 43/40 blends at 23.8° C (75° F). The memory range varied from 57 percent to 107 percent in the 2:1 to approximately the same range in the 4:1 blend.

No data was collected on the (1:4) 25 percent blend due to the excessive reduction in viscosity.

Blends of the 27 percent solutions at 23.8° C (75° F) are presented in Figure 23 with percent memory ranging from 60 to 102 percent. The memory curves for all blends except the 1:1 and 1:4 appear to be smooth curves. The reason for the variation in the other curves could possibly be data scatter; however, all curves are prepared from the average of triplicate runs. Also, the memory curves are not fit by a least squares fit, due to the slopes with increasing shear rate ($\dot{\gamma}_\omega$). (Another possibility of this shape in the curves could be the inhomogeneity noted in the SBR rubbers used in the formulations.) A large variation of the flow curve and reduction of memory at various shear rates is more pronounced in the 0° C (32° F) data of the 4:1 blend as is presented in Figures 26 through 28.

The 23.8° C (75° F) data for the 29 percent blends gave curves showing gradual increase of memory with increasing shear rate, but again showing the slope upward with the 1:2 and 1:4 blends at the 0° C (32° F) temperature.

The 30 percent SBR blends showed basically the same range of percent memory, ranging from 60 percent to 114 percent, with data presented in Figures 21 and 26 at 23.8° C (75° F) and 0° C (32° F), respectively.

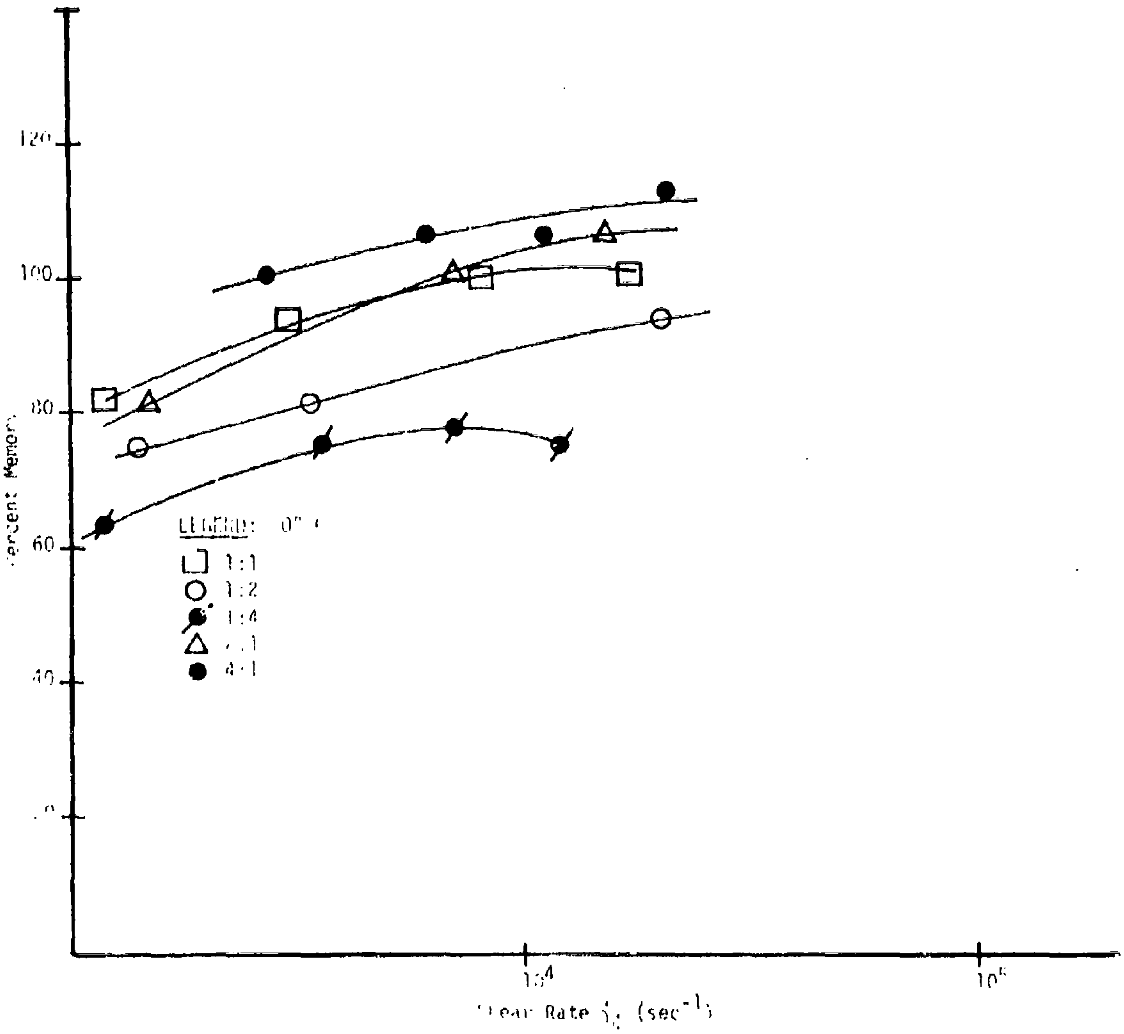

Figure 26. Percent Memory of 30 Percent SBR 43/40 of Various Ratios at 0^o C

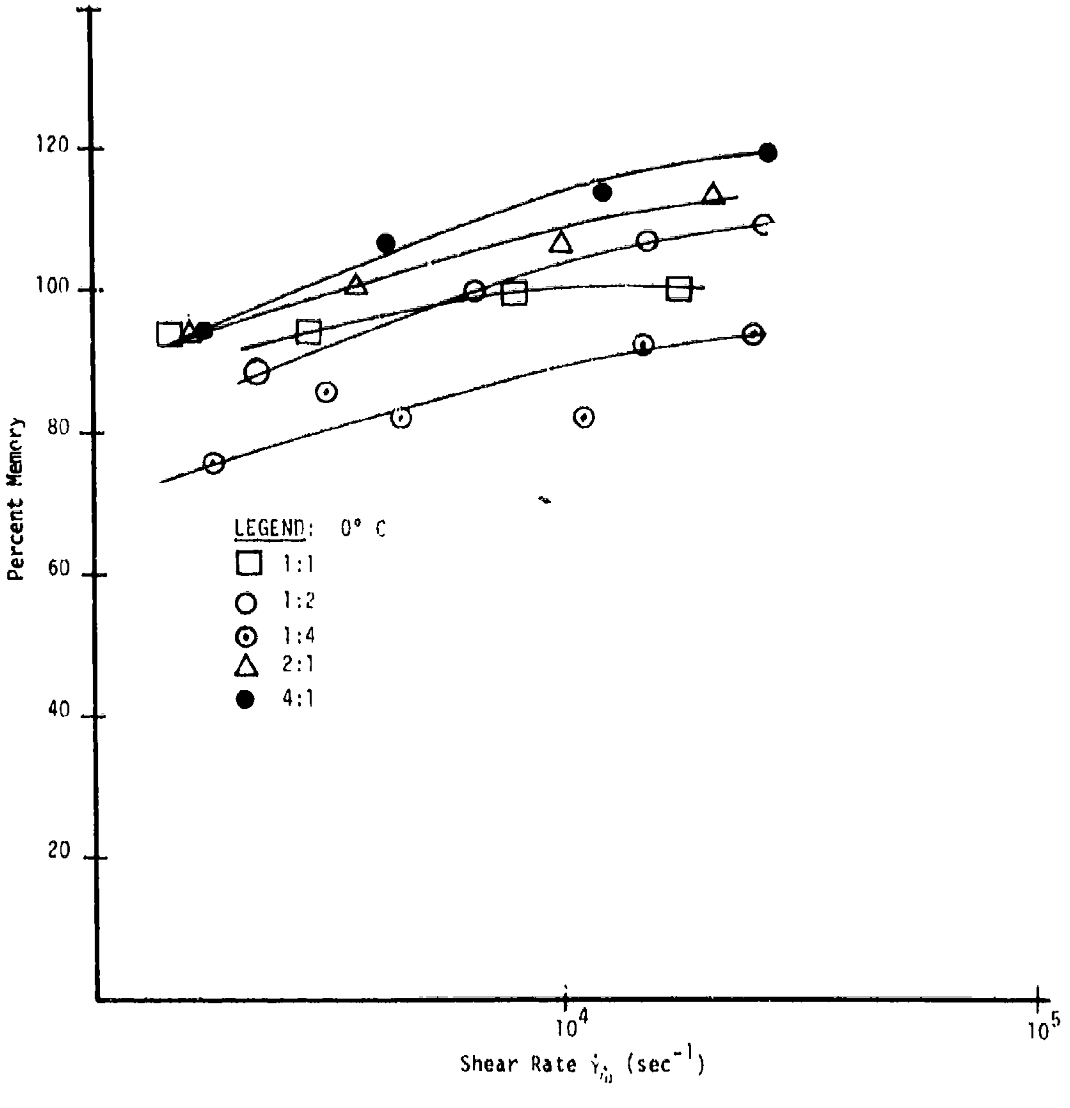

Figure 27. Percent Memory of 29 Percent SBR 43/40 of Various Ratios at 0° C

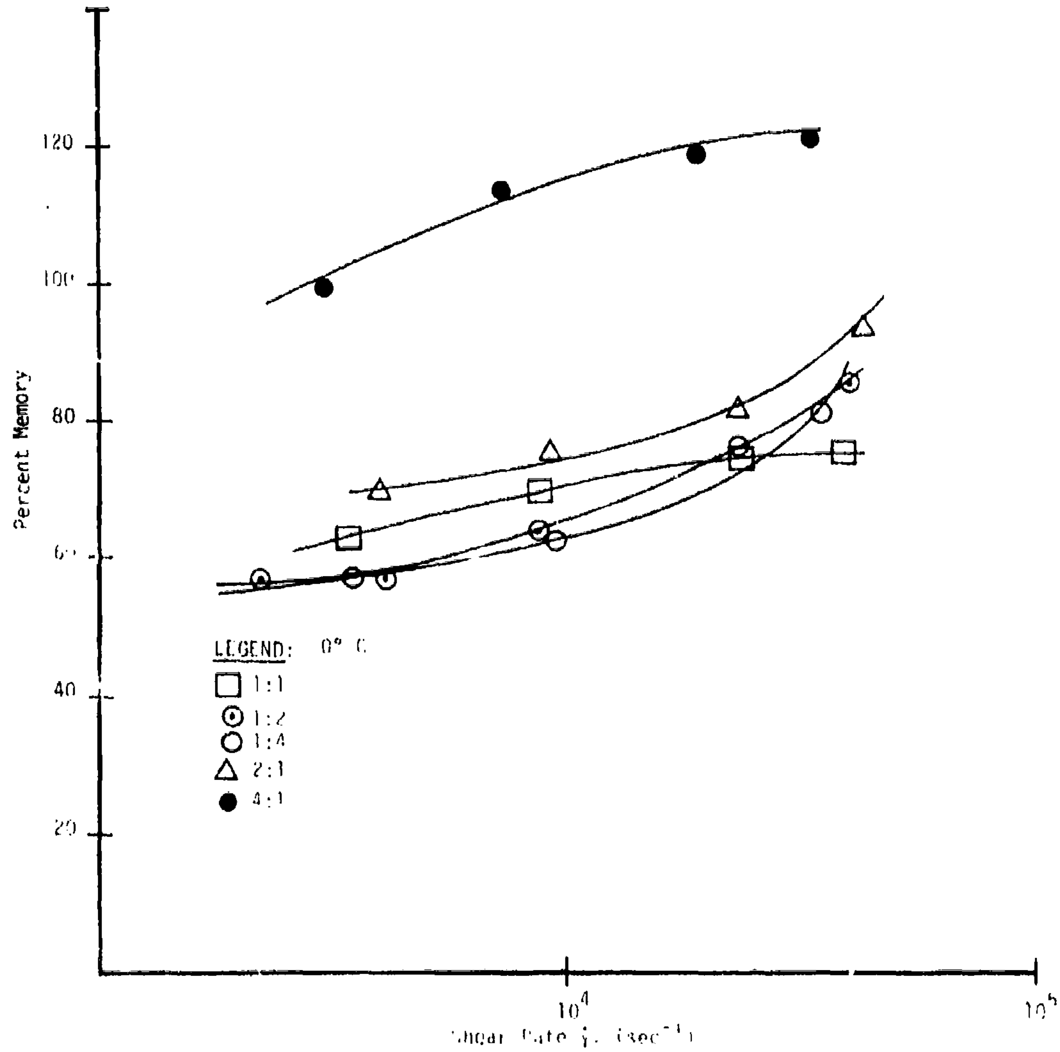

Figure 28. Percent Memory of 27 Percent SBR 43/40 of Various Ratios at 0° C

SECTION IV

AIR GUN EVALUATION OF SBR FORMULATIONS

After the initial screening of flame fuel formulations by rheological testing had been accomplished, a program of aerodynamic testing was begun. This method of evaluation involved the launching of a one pound flame fuel sample from an air gun toward a target board 50 feet away. The behavior of the fuel in the air and on the target at velocities ranging up to 1000 feet per second and at temperatures ranging from -18° to $+30^{\circ}$ C is recorded on high speed movie film. Analysis of the film with regard to the degree of the fuel sample breakup in flight, breakup on impact with the target board, and adhesion of fuel particles to the target board results in the assignment of an effectiveness rating for the fuel at the particular velocity and temperature at which the test was carried out.

Figures 29 through 32 are single frame reproductions of the high speed movie film obtained from the three cameras used on the air gun test range. Figure 29 shows the breakup pattern of a 30 percent SBR 43/40, 2:1 ratio blend during the first 20 feet of flight after the charge is fired. Figure 30 shows the behavior of the flame fuel 40 feet down range, while Figure 31 reveals the flame fuel behavior just before the leading edge contacts the target board. Figure 33 is a still shot of the target board after impact showing the degree of adhesion and the particle size distribution of the flame fuel.

For comparison, Figure 32 depicts the in-flight behavior of Napalm B, the current Air Force inventory flame fuel. Breakup into many fine particles is observed, and it is believed that this situation occurs as a result of the low recoverable shear or inelastic character of the polystyrene solution (Napalm B).

Table 2 presents a summary of the ratings assigned to the various blends of SBR 43/40 at low and normal temperatures and at various velocities. In addition, values for Napalm B and solutions of the pure components of the SBR blends are given. The ratings and velocities listed are an average compiled from three or more shots for the given temperature, polymer percentage, and blend ratio. These ratings indicate that there is very little difference in the behavior of the various blends at low and moderate temperatures, and thus they corroborate the results obtained from the rheological studies.

As a result of these screening studies, the 30 percent SBR 43/40, 2:1 ratio blend was chosen for extensive testing at one-third of full scale on the sled track range.

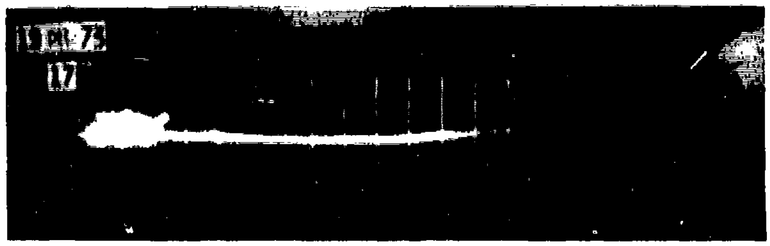

Figure 29. Breakup of SBR 2:1 Blend
Emerging from Air Gun

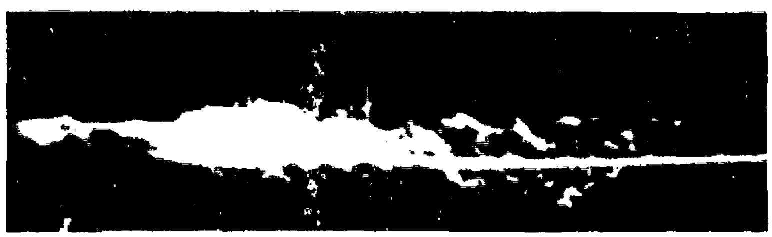

Figure 30. Breakup of SBR 2:1 Blend
40 Feet Down Range

Figure 31. Breakup of SBR 2:1 Blend
Prior to Target Impact

Figure 32. Breakup Pattern of Napalm B - 40 Feet Down Range

Figure 33. SBR 2:1 Target Impact

TABLE 2. AIR GUN TEST RATINGS OF VARIOUS SBR FORMULATIONS AT VARYING SPEEDS AND TEMPERATURES

Percent Sample/Ratio	2:1		1:1		1:2		5:1	
SBR 43/40	Velocity	Rating	Velocity	Rating	Velocity	Rating	Velocity	Rating
27% at 0^{o} F	748	72	754	74	723	76		
28% at 60^{o} F	917	67	834	63	872	63		
29% at 0^{o} F	747	76	721	72	727	66		
29% at 60^{o} F	851	64	857	64	857	59		
30% at 0^{o} F	725	78	750	76	712	75		
30% at 60 F	924	72	888	67	867	65	397 718	84 62
SBR 43 30%	0^{o} F		775 428	75 71				
SBR 40 30%	85^{o} F		795 842	60 50				
Napalm B	0^{o} F		525 500	40				
	50^{o}-60^{o} F		530	63				

SECTION V

SUMMARY

The results of rheological studies on blends of SBR in solution indicate that elastic behavior can be varied considerably without appreciably affecting the viscosity. Temperature changes over the range 0° C to 23° C also have very little effect on viscosity.

Air gun tests indicated the resistance to aerodynamic breakup was improved when the percentage of SBR 43 was increased. Polymer concentration in the range of 27 to 30 percent gave the best results in the aerodynamic testing.

Correlation of results between rheological and air gun tests on samples of the formulations was found to be reasonably close, both at 23.8° C (75° F) and 0° C (32° F).

REFERENCES

1. R. L. Long, Flame Agents for High Velocity/Low Temperature Use, Air Force Armament Laboratory Technical Report AFATL-TR-71-55, May 1971.

2. F. H. Gaskins, Rheological Properties and Performance of Napalm B in Comparison to Standard Flame and Incendiary Agents. Edgewood Arsenal Technical Report EATR 4155, February 1968.

3. E. B. Bagley and H. J. Duffy, Trans. Soc. Rheo. 14:4 545 (1970).

4. Computer Programs for Plastics Engineers, Polymer Technology Series, Society of Plastics Engineers, Rheinhold and Sons, 1968.

5. R. L. Long, Improved Flame Agents, Air Force Armament Laboratory Technical Report AFATL-TR-72-177, September 1972.

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